



Appendix 3 Science Support (Special Studies)

**Municipal Water Quality Investigations
Program 2011-2012 Workplan
4/27/11
Final**

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Appendix 3--Science Support (Special Studies)

Background

The many natural and anthropogenic processes that affect drinking water quality in the Delta, its tributaries, and the State Water Project remain poorly understood. To further improve DWR's ability to measure and forecast drinking water quality of water delivered to its customers, MWQI engages in special studies that focus on specific aspects of source waters, contaminant loading, measurement methods and instrumentation, and climate and hydrology. Results of these studies inform subsequent cycles of the MWQI work plan by improving the RTDF and discrete sampling programs.

Generally strawman proposals of special studies are submitted to the Special Studies subcommittee for discussion and prioritization. Strawman proposals are evaluated on technical merit, how well they meet the needs of the MWQI mission, and funding available to conduct the study.

To keep the workplan concise, only short summary descriptions are provided in the 2011-12 workplan. This appendix contains the full project proposals for some of the special studies that appear in the workplan. In cases where a proposal does not appear in this appendix, the proposal in the workplan did not require further elaboration in this appendix. For some projects, project proposals from earlier workplans are also presented in this appendix. Their inclusion shows the changes and progression of the project from the original proposal to the current study.

2011-12 Workplan Proposal for Urban Sources and Loads Investigation--Lead Investigator: Rachel Pisor

Note that this study proposal updates the 2010-11 study proposal listed in this appendix.

Background/Introduction

The Sacramento/San Joaquin River Delta is a region that had been rapidly growing at a rate much faster than the rest of California and the United States until the housing collapse of the late 2000's. Because of the geographic location of this growth, there is a significant potential for negative effects to drinking water quality. The Delta provides drinking water to approximately 23 million Californians; therefore, the effects of municipal stormwater discharges on water quality are particularly important in this region.

Water quality impacts from urbanization are primarily due to increased urban drainage, increased wastewater discharge, and recreational uses. Increases in the volume of urban drainage are mainly due to increases in impervious cover. Agriculture and open space landscapes are pervious and generally allow for greater percolation of stormwater through the soil. Soils filter contaminants like heavy metals, oil and grease, pesticides, etc., as compared to compacted or developed areas which allow less percolation and more runoff. Urban land uses are mainly characterized by pavement and do not allow water infiltration. Instead, water flows as sheets over the impervious surface to the river. This typically results in higher runoff volumes, with shorter duration but larger magnitude peak flows in response to rainfall. Impervious and semi-impervious (e.g. commercial and residential landscapes) surfaces also catch and store urban contaminants between storm events. Typical urban contaminants include vehicle emissions, vehicle maintenance wastes, landscaping chemicals, household chemicals, pet wastes, and trash. Increases in impervious surfaces and installation of storm sewer systems provide a faster and more direct route for the transport of accumulated pollutants to nearby waterways.

The focus of this study is to analyze the effects of urban drainage on drinking water quality. This will involve analyzing both water quality and land use patterns. This study will be conducted for 3 years.

Background

MWQI began investigating the effects of urban runoff with a study of the Steelhead Creek watershed in the northern Sacramento metropolitan area. Results from that study showed that urban runoff can have significant impacts on drinking water quality and it demonstrated how important tracking this issue is as the Delta continues to urbanize. To further understand these effects, MWQI reviewed several geographic areas for investigation. The City of Lathrop was selected based on accessibility, feasibility and data needs for the San Joaquin River.

Lathrop is a small municipality that was rapidly urbanizing prior to the housing market collapse of the late 2000's. Conversion of agricultural and open space land uses to urban land uses resulted in increased impervious cover. With the collapse of the housing market, this conversion stopped; however, it is anticipated that when the economy rebounds, land use conversion would continue. Therefore, when urbanization resumes, conducting this study today provides a baseline for future studies of the impacts of changing land use on water quality. Also because Lathrop is a small municipality, it is covered under the Phase II General NPDES Permit. This permit does not require Lathrop to monitor its stormwater runoff. In order to manage drinking water throughout the Delta effectively, however, it is necessary to understand the effects of stormwater on drinking water quality from all sizes of growing municipalities.

Objectives

This study will assess the effects of urban stormwater runoff from Lathrop on the San Joaquin River Watershed with special attention paid to first flush events. Because the population of Lathrop is small, this study may serve as a baseline of water quality conditions and land use patterns. As development continues to grow, we will be able to see at what population size urbanization negatively effects drinking water quality. This

may be useful in management decisions regarding monitoring of stormwater and mitigation of negative effects on drinking water quality from urban runoff.

Specifically, this study will quantify background concentrations and loads in the river and loads of specific constituents discharged to the river from the City of Lathrop. Knowing both the background loads in the river and the urban load discharged to the river will provide a relative contribution of urban loading to the river. Using discharge rates and riverine flow measurements, urban and riverine loads will be calculated for nutrients, bromide and organic carbon. Concentration data will be collected for all other constituents. Land use will be analyzed by quantifying the percentage of impervious cover. This will enhance our understanding of water quality effects from urban drainage by linking particular landuses to loads. By linking percent impervious cover to discharges from different landuses, stormwater discharge information from Lathrop may also prove useful in predicting loading from other urban areas.

Study Design

To accomplish the study objectives, we will be collecting water quality samples from Lathrop's stormwater pumping stations. The city's stormwater flows through these pumping stations immediately prior to being discharged to the San Joaquin River. We will also collect river samples to evaluate the proportion of load in the river attributable to urban runoff. We will focus on first flush events because these events have the greatest potential to effect water quality. This will provide a better understanding of what the water quality conditions of the San Joaquin River are and how they are influenced by Lathrop's discharge. In addition, we will collect data from rain gauges to determine precisely how much precipitation occurred during each event.

To complement these analyses, we will use GIS to conduct a land use analysis. All the layers necessary to conduct the analysis will be obtained from the San Joaquin County Assessor's office, the City of Lathrop and the National Agricultural Imagery Program (NAIP).

Stormwater pumping stations

Lathrop handles its stormwater using detention basins and stormwater pumping stations. The detention basins impound the stormwater prior to being conveyed to stormwater pumping stations. Pump stations discharge to the river. Pumping stations are comprised of a wet well, a low-flow pump and up to five main pumps. When water rises to a certain level, the low flow pump turns on. If the water in the wet well continues to rise, and the low flow pump cannot accommodate the flow, the low flow pump will turn off and the main pumps will turn on.

Different regions in Lathrop handle stormwater in different ways. Historic Lathrop does not have a developed stormwater system. Runoff from this region is dealt with by detention basins which channel the water to the River station (figure 1). The Mossdale region of Lathrop has a developed storm drain system which utilizes 5 pumps which discharge to the river. The Stonebridge region utilizes a detention basin and a pumping station. The industrial region of Lathrop uses a detention basin and a pumping station (see figure 1).

Eight Lathrop stormwater pumping stations will be sampled (figure 1). This includes all stations which pump directly to the river and encompasses all the regions of Lathrop. These stations are River Station, Stonebridge, KV, M1, M2, M3, M5, and M6. With the exception of pathogen samples, all pump station samples will be collected by autosamplers (ISCO 3700 or 6712). Because of holding times, pathogen samples will be collected as grab samples.

Frequency of autosampler sample collection will vary by storm size and duration, however samples will be collected as a single composite sample. This sample will be processed according to requirements of the laboratories to analyze the constituents. Further details in sample processing are discussed in the methods section.

Autosampler programming

DWR has hired MCC Consulting to wire the autosamplers into the city's SCADA system at each pumping station. During a rainfall event, the SCADA system monitors the pumps and will trigger autosampler sampling after the pumps have run for a sufficient time to flush out any standing water. This ensures that the water collected by the autosampler reflects the water quality of stormwater runoff, and not the quality of the residual water that has sat in the pipes prior to discharge. With this system in place, the autosamplers will be programmed based on the time that the storm is forecast to begin. This will ensure that the autosampler will not collect any water that is pumped prior to the storm. Each autosampler will be programmed individually based on past pumping records because each pump station has its own pattern of pumping duration and pumping frequency during storm events.

The variation in the storm duration will determine how many sampling events occur for the storm. If the storm only lasts 24 hours, samples will be taken for that 24 hours and then will be processed. If the storm is expected to last for multiple days, the sample will be processed after the first 24 hours and then the autosampler will be re-programmed to collect the samples for the next 24 hour period, after which they would be processed. This pattern will continue up to 3 days worth of samples. After that time it will be decided if it is reasonable to take more samples.

River Station Samples

To assess the load in the river, grab samples at Mossdale (MSD) will be collected. Originally, samples were taken at the San Joaquin River at Lathrop (SJL) and Brandt Bridge (BDT) (see figure 2). After receiving pump data for the second season, it was clear that sampling downstream of discharges was not a good representation of the baseline load plus Lathrop's load due to inconsistent pumping. Additionally, Lathrop contributes approximately 2% of the flow of the San Joaquin River. For these reasons, it was decided that samples should only be collected at the Mossdale station during an ebb tide to give a good representation of the baseline water quality of the San Joaquin River.

All Mossdale station samples will be taken as grab samples the day of the storm. These samples will be processed the same way as the autosampler samples. Due to logistics and availability of staff, there will be only 1 set of river samples taken per storm.

Weather Monitoring and Precipitation Data

Precipitation will be monitored closely throughout the study's duration. Since the focus of this study will be on first flush events, a storm in which 0.5 inches of precipitation is predicted will be sampled if it follows a dry period of 30 days or more. If there is a major storm event within a 30 day dry period, sampling would also occur. For the purpose of this study, a major storm event is defined as storm producing 1.5+ inches of precipitation over a 24 hour period. These are general guidelines for sampling protocol and it is possible that storm sampling may be modified.

At two of the stormwater lift stations, rain gauges are installed. These are RainWise 8 - inch diameter tipping bucket rain gauges equipped with dataloggers. One is located at the Stonebridge station and the other is at the River station. These rain gauges will store up to 365 days worth of data and record data every minute. The two gauges installed are geographically separated to account for regional differences in precipitation.

Flow Data

One of the focuses of this study will be to make a determination of carbon, bromide and nutrient load. Load is a function of concentration and flow. The river stations have continuous flow data; however, there is no continuous flow data at the autosampler stations. Flow data at these sites will be determined by the pump rating curves. By knowing the pump rates and duration of pumping, we will calculate the approximate flow during sampling events.

Methods

Processing of water quality samples

Physical parameters

Physical parameters will be taken in the field as soon as possible after collection.

Physical parameters measured will include dissolved oxygen, pH, electrical conductivity, temperature and turbidity.

Samples prepared for Bryte Laboratory

All the samples prepared for Bryte laboratory will be processed in accordance with the laboratory's guidelines. This includes filtration, acidification, and agitation of the matrix when applicable. All samples will be put on ice until returned to the lab.

Pathogen samples

Pathogen samples will always be collected as grab samples and will be taken at the San Joaquin River sampling site and the autosampler stations. These samples cannot be collected from an autosampler due to the probability of bacteria death or reproduction during the time between collection and processing. Immediately after collection, pathogen samples will be put on ice and delivered to the FGL Laboratory within the 6-hour holding time. FGL Laboratory is subcontracted through Weck Laboratory which is contracted through the Department.

Replicate TTHMFP and HAAFP samples

Additional samples for total trihalomethane formation potential (TTHMFP) and haloacetic acid formation potential (HAAFP) will be collected and sent to Weck Laboratory the day after collection. The samples collected will be unfiltered, but they will be filtered using a 0.45 micron filter in laboratory prior to processing. The results of these additional samples will be used to compare Bryte lab's DWR modified TTHMFP and HAAFP method to Weck Laboratory's method, SM 5710B.

Duplicate and Replicate Samples

During each sampling event, replicate samples will be taken for all constituents at the River Station or M5 with the exception of pathogens. Originally, M5 was the replicate station, but was changed to the River station due to complications with the M5 pump station. The replicate sample is collected from an autosampler outfitted with a 19-L glass jar. All other autosamplers are outfitted with a 9-L glass jar. Nine liters is a sufficient volume to collect sample for all the analyses, but not sufficient to collect sample for replicates. Due to the large size of the 19-L jar and the complex set up at each of the stations, frequently switching out this jar with other stations is not feasible. Both the regular sample and replicate sample will be collected from the same 19 liter container. During each event, pathogen sample duplicates will be taken. The duplicate station will rotate among the autosampler stations. The duplicate is a second sample taken directly from the water source and the sample method is identical to that of the parent sample. For a complete list of analyses and methods, see Table 1.

Analysis of Loads

Load calculations will be computed for nutrients, bromide and organic carbon. Loads are a function of flow and concentration and can be computed as the integral of the instantaneous discharge multiplied by the concentration for a defined time period (dt):

$$L = \int_0^t K \cdot Q_t \cdot C_t dt$$

Where L is load for interval 0 to t, K is a unit conversion factor, Q_t is the instantaneous discharge, C_t is instantaneous concentration (Coats, 2002). Because the data we will be collecting from the pumping stations is not in real time for all flows and concentrations, we will compute loads as the product of the average flow and the average concentration for a defined time period:

$$L_{0-t} = \bar{Q}_{0-t} \cdot \bar{C}_{0-t}$$

Where L_{0-t} is load from time interval 0 to t, \bar{Q}_{0-t} is the average flow from 0 to t and \bar{C}_{0-t} is the average concentration from 0 to t.

For the Mossdale station, we be collecting a grab sample and therefore we will not be using averages to compute the load. For these stations, we will be computing an instantaneous load at time (t):

$$L_t = Q_t \cdot C_t$$

Where L_t is the load at time t, Q_t is the flow at time t and C_t is the concentration at time t.

Data Analysis

For all analytes, statistical comparisons using either concentration or load values (if calculated) will be used. Statistical comparisons will be used to examine significant differences in trends or seasonality between stations, storms and water years. Analyses will include examining differences between grab samples from the river stations and the 8 pumping stations, between the regions in Lathrop and between the individual storms. An ANOVA will be used for these analyses if the data is normally distributed. If the data is not normally distributed, the non-parametric Kruskal-Wallis and Mann-Whitney tests will be used. A trends analysis will determine if there are statistically significant trends over the course of the wet season or between years. If the data follows a normal distribution, a regression based on time will be used. If the data is not normally distributed, a Mann-Kendall test will be used.

Figure 1. Map of the study area. Note that the Historic Region is pumped by the River Station

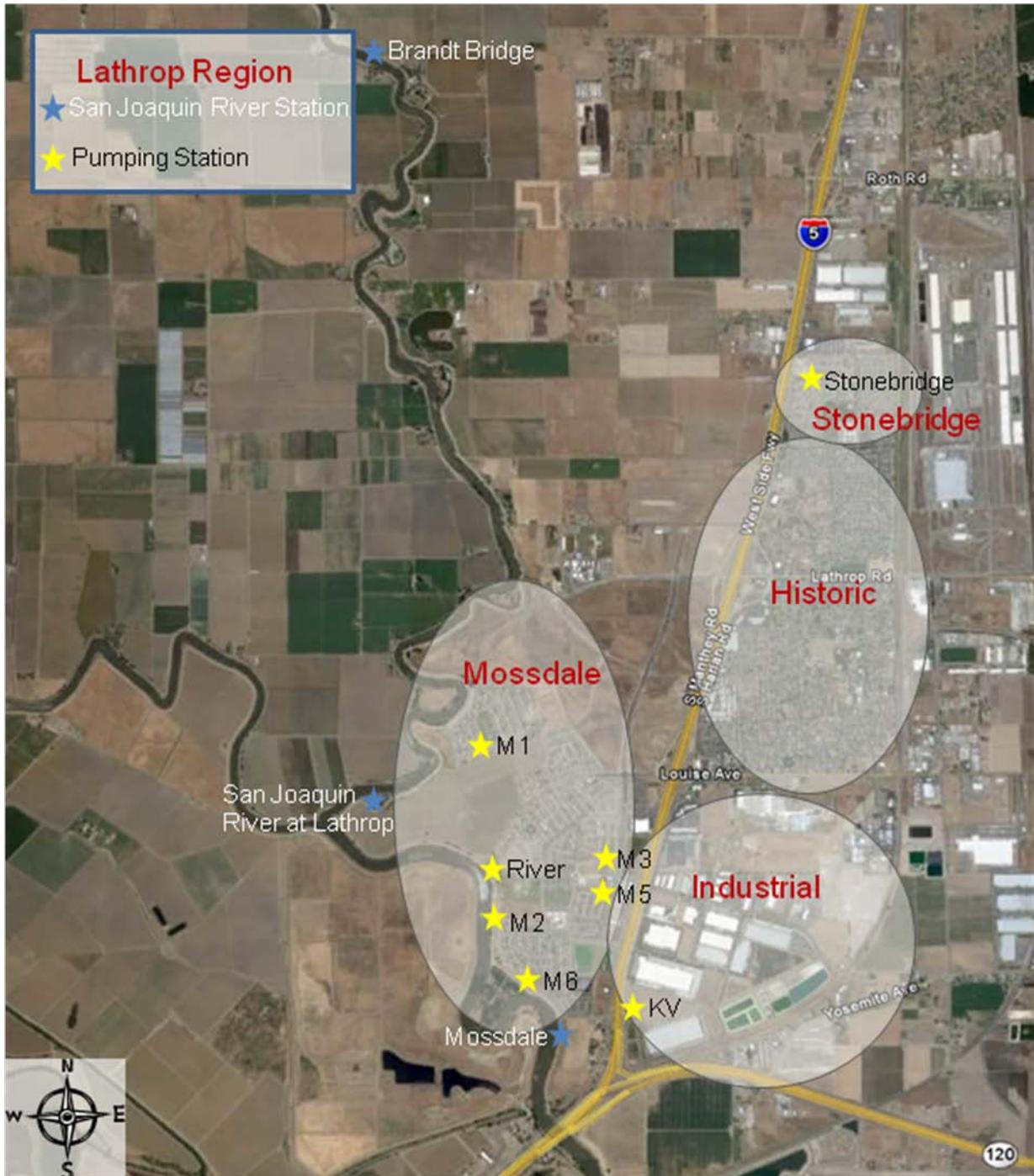


Table 1 Laboratory Analyses and Methods

Method	Analyte
Std Method 2340 B, Hardness By Calculation	All
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Calcium
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Magnesium
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Potassium
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Sodium
EPA 300.0 28d Hold, Inorganic Anions 28d hold	Dissolved Sulfate
EPA 300.0 28d Hold, Inorganic Anions 28d hold	Dissolved Chloride
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Boron
Std Method 2540 C, Total Dissolved Solids (TDS)	All
Std Method 2320 B, Alkalinity	All
Std Method 2510-B, Electrical Conductivity (EC)	All
EPA 300.0 28d Hold, Inorganic Anions 28d hold	Dissolved Nitrate
Std Method 4500-NO3-F (28Day), Nitrite, Nitrate (DWR Modified)	Dissolved Nitrate + Nitrite
EPA 350.1, Ammonia, Nitrogen (Dissolved)	All
EPA 351.2, Kjeldahl Nitrogen	All
EPA 365.1 (DWR Modified), DWR Othro-Phosphate (Dissolved)	All
EPA 365.4, Phosphorus (Total)	All
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Silver
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Aluminum
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Antimony
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Arsenic
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Cadmium
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Nickel
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Zinc
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Selenium
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Molybdenum
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Manganese
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Lead
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Copper
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Iron
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Lead
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Copper
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Chromium
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Aluminum
EPA 415.1 (D) Ox, Organic Carbon (Dissolved) by Wet Oxidation	All
EPA 415.1 (T) Ox, Organic Carbon (Total) by Wet Oxidation	All
Std Method 5910B, UVA	All
EPA 608, Chlorinated Organic Pesticides	All
EPA 614, Phosphorus / Nitrogen Pesticides	All
EPA 160.2, Total Suspended Solids	Total Suspended Solids
DWR THMFP (Buffered), DWR THMFP (Buffered)	All
DWR HAAFP (Buffered), Haloacetic Acid Formation Potentials	All
Std Method 9221B,E, Total and Fecal Coliform ₁	All
Std Method 9223B, Total and E.Coli Coliform ₁	All
GC/MS NCI-SIM, Pyrethroid Pesticides ₂	All
Std Method SM 5710B, THMFP, HAAFP ₂	All

₁Analysis conducted by FGL Laboratory, Stockton, Ca

₂Analysis conducted by Weck Laboratory, City of Industry, Ca

Deliverables and Timelines

Deliverables	Participants	Estimated Start Date	*Estimated Completion Date
Storm event sampling at 11 sites in the Lathrop study area	MWQI Program MWQI Field Group	Winter 2009	July 2012
Analysis of samples as indicated above by DWR	Bryte Laboratory	Winter 2009	August 2012
Analysis of samples as indicated above through contract with Weck	FGL Laboratory	Winter 2009	August 2012
Analysis of samples as indicated above through contract with Weck	Weck Laboratory	Winter 2009	August 2012
Final Report	MWQI Program	September 2011	April 2013

* Note that based on potential summer storm events, sample completion dates are tentative. The estimated sample completion date of July 2012 includes the possibility of rare summer storm events. Final deadlines will be adjusted based on when actual storm events end in water year 2012.

Literature Cited

Coats, R.N., F. Liu, and C.R. Goldman. 2002 A Monte Carlo test of Load Calculation Methods, Lake Tahoe Basin, California-Nevada. *Journal of the American Water Resources Association* 38(3): 719-730.

Budget

See 2011/2012 Workplan

2010-11 Workplan Proposal for Urban Sources and Loads Investigation--Lead Investigator: Rachel Pisor

Note that this study proposal updates the 2009-10 study proposal listed in this appendix.

Background/Introduction

The Sacramento/San Joaquin River Delta is a region that has been rapidly growing at a rate much faster than the rest of California and the United States. Because of the geographic location of this growth, there is a significant potential for negative effects to drinking water quality. The Delta provides drinking water to approximately 25 million Californians; therefore, the effects of municipal stormwater discharges on water quality are particularly important in this region.

Water quality impacts from urbanization are primarily due to increased urban drainage, increased wastewater discharge, and recreational uses. Increases in the volume of urban drainage are mainly due to increases in impervious cover. Agriculture and open space landscapes are pervious and generally allow for greater percolation of stormwater through the soil. Soils filter contaminants like heavy metals, oil and grease, pesticides, etc., as compared to compacted or developed areas which allows less percolation and more runoff. Urban land uses are mainly characterized by pavement and do not allow water infiltration. Instead, water flows as sheets over the impervious surface to the river. This typically results in higher runoff volumes, with shorter duration but larger magnitude peak flows in response to rainfall. Impervious and semi-impervious (e.g. commercial and residential landscapes) surfaces also catch and store urban contaminants between storm events. Typical urban contaminants include vehicle emissions, vehicle maintenance wastes, landscaping chemicals, household chemicals, pet wastes, and trash. Increases in impervious surfaces and installation of storm sewer systems provide a faster and more direct route for the transport of accumulated pollutants to nearby waterways.

The focus of this study is to analyze the effects of urban drainage on drinking water quality. This will involve analyzing both water quality and land use patterns. This study

will be conducted for 2 years. At the end of this time, MWQI will determine whether additional sampling is necessary.

Background

MWQI began investigating the effects of urban runoff with a study of the Steelhead Creek watershed in the northern Sacramento metropolitan area. Results from that study showed that urban runoff can have significant impacts on drinking water quality and it demonstrated how important tracking this issue is as the Delta continues to urbanize. To further understand these effects, MWQI reviewed several geographic areas for investigation. We considered northern and southern Sacramento, Stockton, Brentwood, Lathrop and Mountain House, but selected the City of Lathrop based on accessibility, feasibility and data needs for the San Joaquin River.

Lathrop is a small municipality that was rapidly urbanizing prior to the housing market collapse of the late 2000's. Conversion of agricultural and open space land uses to urban land uses resulted in increased impervious cover. With the collapse of the housing market, this conversion stopped, however, it is anticipated that when the economy rebounds, land use conversion would continue. Therefore, when urbanization resumes, conducting this study today provides a baseline for future studies of the impacts of changing land use on water quality. Also because Lathrop is a small municipality, it is covered under the Phase II General NPDES Permit. This permit does not require Lathrop to monitor its stormwater runoff. In order to manage drinking water throughout the Delta effectively, however, it is necessary to understand the effects of stormwater on drinking water quality from all sizes of growing municipalities.

Objectives

This study will assess the effects of urban stormwater runoff from Lathrop on the San Joaquin River Watershed with special attention paid to first flush events. Because the population of Lathrop is small, this study may serve as a baseline of water quality conditions and land use patterns. As development continues to grow, we will be able to see at what population size urbanization negatively effects drinking water quality. This

may be useful in management decisions regarding monitoring of stormwater and mitigation of negative effects on drinking water quality from urban runoff.

Specifically, this study will quantify background concentrations and loads in the river and loads of specific constituents discharged to the river from the City of Lathrop. Knowing both the background loads in the river and the urban load discharged to the river will provide a relative contribution of urban loading to the river. Using discharge rates and riverine flow measurements, urban and riverine loads will be calculated for nutrients and organic carbon. Concentration data will be collected for all other constituents. Land use will be analyzed by quantifying the percentage of impervious cover. This will enhance our understanding of water quality effects from urban drainage by linking particular landuses to loads. By linking percent impervious cover to discharges from different landuses, stormwater discharge information from Lathrop may also prove useful in predicting loading from other urban areas.

Study Design

To accomplish the study objectives, we will be collecting water quality samples from Lathrop's stormwater pumping stations. The city's stormwater flows through these pumping stations immediately prior to being discharged to the San Joaquin River. We will also collect river samples upstream and downstream of Lathrop's discharge to evaluate the proportion of load in the river attributable to urban runoff. We will focus on first flush events because these events have the greatest potential to effect water quality. This will provide a better understanding of what the water quality conditions of the San Joaquin River are and how they are influenced by Lathrop's discharge. In addition, we will collect data from rain gauges to determine precisely how much precipitation occurred during each event.

To complement these analyses, we will use GIS to conduct a land use analysis. All the layers necessary to conduct the analysis will be obtained from the San Joaquin County Assessor's office.

Stormwater pumping stations

Lathrop handles its stormwater using detention basins and stormwater pumping stations. The detention basins impound the stormwater prior to being conveyed to stormwater pumping stations. Pump stations discharge to the river. Pumping stations are comprised of a wet well, a low-flow pump and up to three main pumps. When water rises to a certain level, the low flow pump turns on. If the water in the wet well continues to rise, and the low flow pump cannot accommodate the flow, the low flow pump will turn off and the main pumps will turn on.

Different regions in Lathrop handle stormwater in different ways. Historic Lathrop does not have a developed stormwater system. Runoff from this region is dealt with by detention basins which channel the water to the River station (figure 1). The Mossdale region of Lathrop has a developed storm drain system which utilizes 5 pumps which discharge to the river. The Stonebridge region utilizes a detention basin and a pumping station. The industrial region of Lathrop uses a detention basin and a pumping station (see figure 1).

Eight Lathrop stormwater pumping stations will be sampled (see figure 2). This includes all stations which pump directly to the river and encompasses all the regions of Lathrop. These stations are River Station, Stonebridge, KV, M1, M2, M3, M5, and M6. With the exception of pathogen samples, all pump station samples will be collected by autosamplers (ISCO 3700 or 6712). Because of holding times, pathogen samples will be collected as grab samples.

Frequency of autosampler sample collection will vary by storm size and duration, however samples will be collected as a single composite sample. This sample will be processed according to requirements of the laboratories to analyze the constituents. For further details in sample processing, see the methods section.

SCADA programming for Autosampler sampling

DWR has hired MCC Consulting to wire the autosamplers into the city's SCADA system at each pumping station. During a rainfall event, the SCADA system monitors the pumps and will trigger autosampler sampling after the pumps have run for a sufficient time to flush out any standing water. This ensures that the water collected by the autosampler reflects the water quality of stormwater runoff, and not the quality of the residual water that has sat in the pipes prior to discharge. The SCADA system will send a text message to a cell phone when the first signal has been sent to the autosampler to collect a sample. This will alert staff that sampling has begun and allow efficient staging for sample deployment.

Manual programming for Autosampler sampling

In the event that the SCADA system is not operational, autosamplers will be manually programmed to collect samples at pre-determined intervals. Prior to a rainfall event, weather will be closely monitored and the autosamplers manually programmed. Autosamplers will be programmed identically. To ensure that samples are collected after residual water has been flushed from the discharge system, autosamplers will be programmed to begin sampling after the storm has begun. At most stations a 10-15 minute delay is sufficient to ensure that residual water is flushed from the pipes. In addition to allowing residual flushing of standing water, delayed start times also ensures that enough water has collected in the stilling well to allow sample collected. Since the volume of water in the stilling well is dependent on the volume of stormwater runoff, delayed start times will also have to factor in the intensity of the storm to ensure that enough water has collected in the stilling wells to ensure adequate volume for sampling. If a storm is predicted to last multiple days, the samples will be switched out every 24 hours. The whole suite of samples will be processed for each day of the storm.

Weather based Autosampling frequency and duration

The variation in the storm will determine how many samples are collected from each autosampler. If the storm only lasts 24 hours, samples will be taken for that 24 hours and then will be processed. If the storm is expected to last for multiple days, the processing

will change. After the first 24 hours, the water will be collected and processed. If the storm is expected to continue for another full day, then the autosampler will be re-programmed to collect the samples for the next 24 hour period, after which they would be processed. This pattern will continue up to 3 days worth of samples. After that time it will be decided if it is reasonable to take more samples.

River Station Samples

To assess the load in the river, grab samples will be taken above and below Lathrop on the San Joaquin River. Sample will be collected at Mossdale (MSD), San Joaquin River at Lathrop (SJL), and Brandt Bridge (BDT) (see figure 2). Originally, samples were also scheduled to be collected from the Head of Old River (OH1), but this station has been removed for safety and logistical reasons.

This region of the Delta is tidally influenced and therefore it is necessary to consider tidal cycles when collecting and analyzing the data so that they are comparable. When there is an ebb tide, the water is flowing from the Delta out to sea. In this case, we would sample at MSD first, then SJL and finally BDT. The MSD sample would serve as the background condition and the BDT sample would serve as the background plus what Lathrop has contributed. If the tide is a flood tide, the water will flow from the sea into the Delta. In this case, we would first sample at BDT, then SJL, and finally MSD. In this case, BDT is the background condition and MSD is the background plus what Lathrop has contributed. Tide prediction software, Tides & Currents Pro, will be used to monitor the tides and will be used as a tool to help make decisions about sampling times for the river stations.

All river station samples will be taken as grab samples the day of the storm. These samples will be processed the same way as the autosampler samples.

Weather and River Station Samples

River samples, like autosampler samples, will be taken during storm events. These grab samples will be taken during the first day of the storm to catch first flush effects. Due to logistics and availability of staff, there will be only 1 set of river samples taken per storm.

Weather Monitoring and Precipitation Data

Precipitation will be monitored closely throughout the study's duration. Since the focus of this study will be on first flush events, a storm in which 0.5 inches of precipitation is predicted will be sampled if it follows a dry period of 30 days or more. If there is a major storm event within a 30 day dry period, sampling would also occur. For the purpose of this study, a major storm event is defined as storm producing 1.5+ inches of precipitation over a 24 hour period. These are general guidelines for sampling protocol and it is possible that storm sampling may be modified.

At two of the stormwater lift stations, rain gauges are installed. These are RainWise 8 - inch diameter tipping bucket rain gauges equipped with dataloggers. One is located at the Stonebridge station and the other is at the River station. These rain gauges will store up to 365 days worth of data and record data every minute. The two gauges installed are geographically separated to account for regional differences in precipitation.

Flow Data

One of the focuses of this study will be to make a determination of carbon and nutrient load. Load is a function of concentration and flow. The river stations have continuous flow data; however, there is no continuous flow data at the autosampler stations. Flow data at these sites will be determined by the pump rating curves. By knowing the pump rates and duration of pumping, we will calculate the approximate flow during sampling events.

Methods

Processing of water quality samples

Physical parameters

Physical parameters will be taken in the field as soon as possible after collection.

Physical parameters measured will include dissolved oxygen, pH, electrical conductivity, temperature and turbidity.

Samples prepared for Bryte Laboratory

All the samples prepared for Bryte laboratory will be processed in accordance with the laboratory's guidelines. This includes filtration, acidification, and agitation of the matrix when applicable. All samples will be put on ice until returned to the lab.

Pathogen samples

Pathogen samples will always be collected as grab samples and will be taken at the river sampling sites and autosampler stations. These samples cannot be collected from an autosampler due to the probability of bacteria death or reproduction during the time between collection and processing. Immediately after collection, pathogen samples will be put on ice and delivered to the FGL Laboratory within the 6-hour holding time. FGL Laboratory is subcontracted through Weck Laboratory which is contracted through the Department.

Replicate TTHMFP and HAAFP samples

Additional samples for total trihalomethane formation potential (TTHMFP) and haloacetic acid formation potential (HAAFP) will be collected and sent to Weck Laboratory the day after collection. The samples collected will be unfiltered, but they will be filtered using a 0.45 micron filter in laboratory prior to processing. The results of these additional samples will be used to compare Bryte lab's DWR modified TTHMFP and HAAFP method to Weck Laboratory's method, SM 5710B.

Duplicate and Replicate Samples

During each sampling event, replicate samples will be taken for all constituents at station M5 with the exception of pathogens. At M-5, the autosampler is outfitted with a 19-L glass jar. All other stations are outfitted with a 9-L glass jar. Nine liters is a sufficient volume to collect sample for all the analyses, but not sufficient to collect sample for replicates. Due to the large size of the 19-L jar and the set up at each of the stations, switching out this jar with other stations is not feasible. Both the regular sample and replicate sample will be collected from the same 19 liter container.

During each event, pathogen sample duplicates will be taken. The duplicate station will rotate among the autosampler stations. The duplicate is a second sample taken directly from the water source and sample method is identical to that of the parent sample. For a complete list of analyses and methods, see Table 1.

Analysis of Loads

Load calculations will be computed for nutrients and organic carbon. Loads are a function of flow and concentration and can be computed as the integral of the instantaneous discharge multiplied by the concentration for a defined time period (dt):

$$L = \int_0^t K \cdot Q_t \cdot C_t dt$$

Where L is load for interval 0 to t, K is a unit conversion factor, Q_t is the instantaneous discharge, C_t is instantaneous concentration (Coats, 2002). Because the data we will be collecting from the pumping stations is not in real time for all flows and concentrations, we will compute loads as the product of the average flow and the average concentration for a defined time period:

$$L_{0-t} = \bar{Q}_{0-t} \cdot \bar{C}_{0-t}$$

Where L_{0-t} is load from time interval 0 to t, \bar{Q}_{0-t} is the average flow from 0 to t and \bar{C}_{0-t} is the average concentration from 0 to t.

For the river stations, we be collecting a grab sample and therefore we will not be using averages to compute the load. For these stations, we will be computing an instantaneous load at time (t):

$$L_t = Q_t \cdot C_t$$

Where L_t is the load at time t, Q_t is the flow at time t and C_t is the concentration at time t.

Data Analysis

Load will be calculated for organic carbon and nutrients. For all other analytes, statistical comparisons using either concentration or load values will be used. Statistical comparisons will be used to examine significant differences in trends or seasonality between stations, storms and water years. Analyses will include examining differences between upstream and downstream points on the rivers, between grab samples from the river stations and the 8 pumping stations and between the individual storms. An ANOVA will be used for these analyses if the data is normally distributed. If the data is not normally distributed, the non-parametric Kruskal-Wallis test will be used. A trends analysis will determine if there are statistically significant trends over the course of the wet season or between years. If the data follows a normal distribution, a regression based on time will be used. If the data is not normally distributed, a Mann-Kendall test will be used.

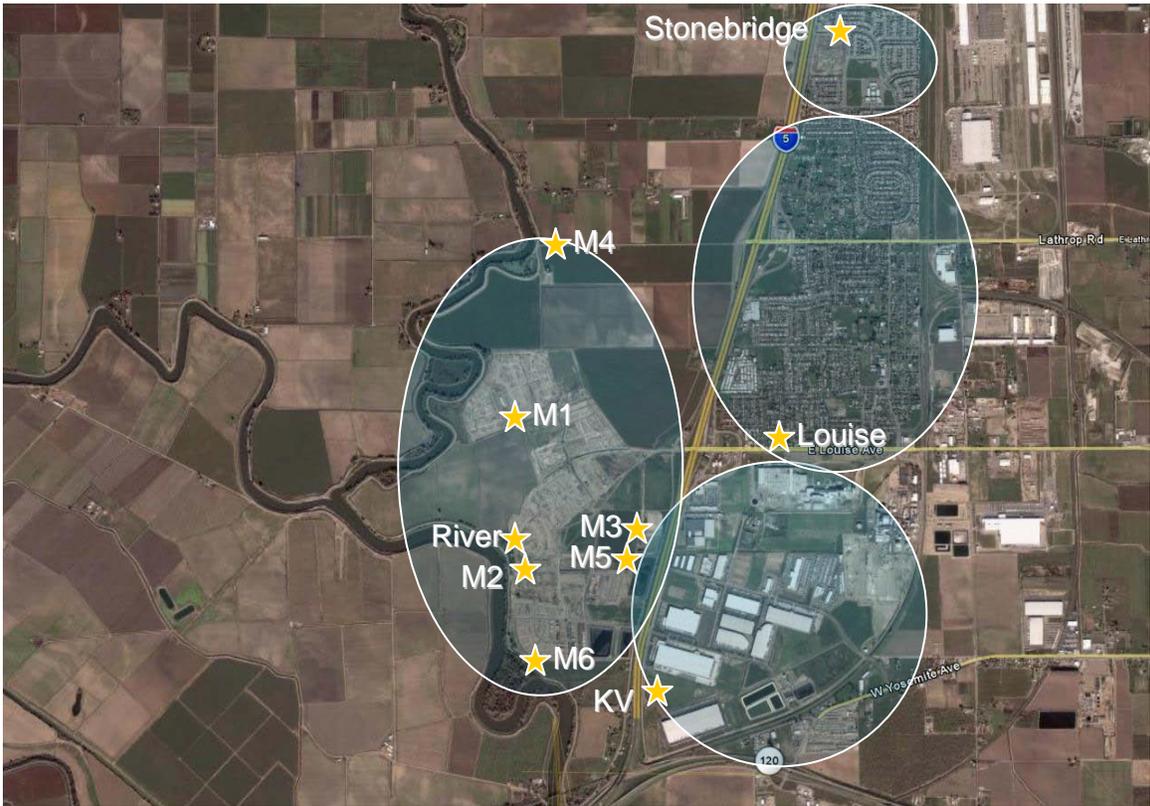


Figure 1. Approximate Regions of Lathrop handled by different stormwater pumping stations. Note that the Louise Station pumps water directly from historic Lathrop to the River Station.

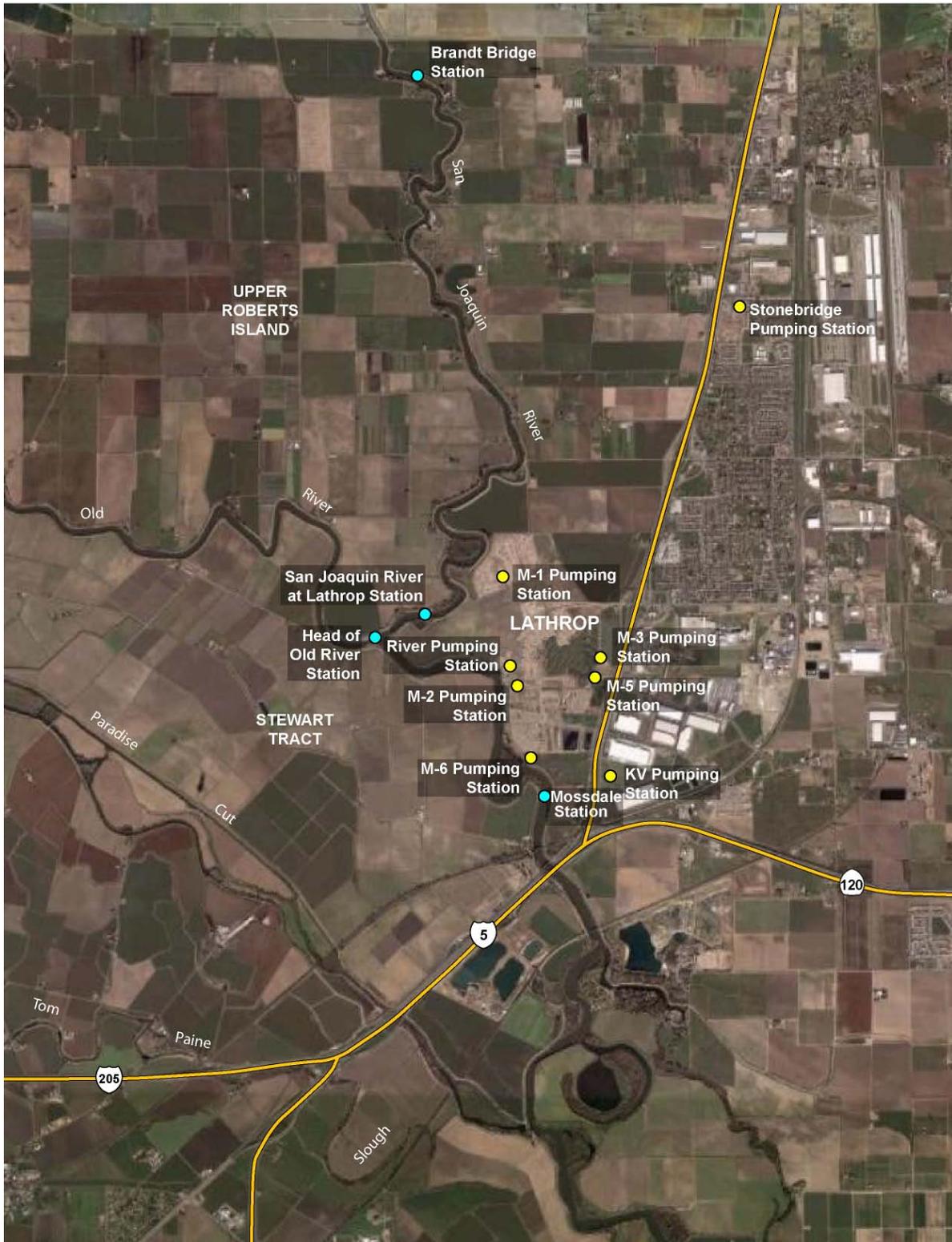


Figure 2. Location of sampling stations for Lathrop Urban Drainage Study. City discharge pump stations are in yellow. River sampling stations are in blue.

Table 1 Laboratory Analyses and Methods

Method	Analyte
Std Method 2340 B, Hardness By Calculation	All
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Calcium
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Magnesium
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Potassium
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Sodium
EPA 300.0 28d Hold, Inorganic Anions 28d hold	Dissolved Sulfate
EPA 300.0 28d Hold, Inorganic Anions 28d hold	Dissolved Chloride
EPA 200.7 (D), ICP Metals and Trace Elements (Dissolved)	Dissolved Boron
Std Method 2540 C, Total Dissolved Solids (TDS)	All
Std Method 2320 B, Alkalinity	All
Std Method 2510-B, Electrical Conductivity (EC)	All
EPA 300.0 28d Hold, Inorganic Anions 28d hold	Dissolved Nitrate
Std Method 4500-NO3-F (28Day), Nitrite, Nitrate (DWR Modified)	Dissolved Nitrate + Nitrite
EPA 350.1, Ammonia, Nitrogen (Dissolved)	All
EPA 351.2, Kjeldahl Nitrogen	All
EPA 365.1 (DWR Modified), DWR Othro-Phosphate (Dissolved)	All
EPA 365.4, Phosphorus (Total)	All
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Silver
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Aluminum
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Antimony
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Arsenic
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Cadmium
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Nickel
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Zinc
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Selenium
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Molybdenum
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Manganese
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Lead
EPA 200.8 (D), ICP/MS Trace Elements (Dissolved)	Dissolved Copper
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Iron
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Lead
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Copper
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Chromium
EPA 200.8 (T), ICP/MS Trace Elements (Total)	Total Aluminum
EPA 415.1 (D) Ox, Organic Carbon (Dissolved) by Wet Oxidation	All
EPA 415.1 (T) Ox, Organic Carbon (Total) by Wet Oxidation	All
Std Method 5910B, UVA	All
EPA 608, Chlorinated Organic Pesticides	All
EPA 614, Phosphorus / Nitrogen Pesticides	All
EPA 160.2, Total Suspended Solids	Total Suspended Solids
DWR THMFP (Buffered), DWR THMFP (Buffered)	All
DWR HAAFP (Buffered), Haloacetic Acid Formation Potentials	All
Std Method 9221B,E, Total and Fecal Coliform ₁	All
Std Method 9223B, Total and E.Coli Coliform ₁	All
GC/MS NCI-SIM, Pyrethroid Pesticides ₂	All
Std Method SM 5710B, THMFP, HAAFP ₂	All

₁Analysis conducted by FGL Laboratory, Stockton, Ca

₂Analysis conducted by Weck Laboratory, City of Industry, Ca

Deliverables and Timelines

Deliverables	Participants	Estimated Start Date	*Estimated Completion Date
Storm event sampling at 11 sites in the Lathrop study area	MWQI Program MWQI Field Group	Winter 2009	July 2011
Analysis of samples as indicated above by DWR	Bryte Laboratory	Winter 2009	August 2011
Analysis of samples as indicated above through contract with Weck	FGL Laboratory	Winter 2009	August 2011
Analysis of samples as indicated above through contract with Weck	Weck Laboratory	Winter 2009	August 2011
Final Report	MWQI Program	September 2011	April 2012

* Note that based on potential summer storm events, sample completion dates are tentative. The estimated sample completion date of July 2011 includes the possibility of rare summer storm events. Final deadlines will be adjusted based on when actual storm events end in water year 2011.

Literature Cited

Coats, R.N., F. Liu, and C.R. Goldman. 2002 A Monte Carlo test of Load Calculation Methods, Lake Tahoe Basin, California-Nevada. Journal of the American Water Resources Association 38(3): 719-730.

Budget

See 2010/2011 Workplan

2009-10 Workplan Proposal for Urban Sources and Loads Investigation--Lead Investigator: Rachel Pisor

Note that this study proposal updates the 2008-09 study proposal listed in this appendix

Background/Introduction

As urbanization in the Delta increases, so does the potential for impacts to drinking water quality. MWQI began to investigate the effects of urban runoff with a study of the Steelhead Creek watershed. Results from that study showed that urban runoff can have significant impacts to drinking water quality and demonstrated how important tracking this issue is as the Delta continues to urbanize. To further understand these effects, MWQI reviewed several areas of concern for further investigation. Under consideration were northern and southern Sacramento, Stockton, Brentwood, Lathrop and Mountain House.

A northern Sacramento area study would revisit the Steelhead Creek study to assess changes in land use and water quality. Since the completion of that study, there has been a major collapse in the housing market; therefore, any further changes in land use and water quality are unlikely. In southern Sacramento, Morrison Creek flows to the Sacramento, Mokelumne, and Cosumnes Rivers. During storm events, water backs up into Beach Lake, preventing accurate calculations of the volume and quality of water that flows to the Sacramento, therefore, making this site infeasible.

There is much interest in focusing on the San Joaquin River watershed especially considering the current pumping restrictions. In Stockton, numerous creeks and sloughs drain into the San Joaquin River; however, they are geographically widespread, making this site logistically infeasible. Additionally, some of the sloughs drain both agriculture and urban land, making it impossible to differentiate between urban and agricultural runoff. Finally, not all Stockton runoffs flow to the San Joaquin River. Therefore, smaller municipalities of Brentwood, Mountain House and Lathrop were considered.

Brentwood's runoff flows northerly to Big Break and out to San Pablo Bay and does not influence drinking water quality. Mountain House was considered and was logistically sound, but due to current pumping schedules, runoff from Mountain House would flow more directly to the Central Valley Project through the Delta Mendota Canal than to the State Water Project. Lathrop was determined to be the best choice for this study because its location is logistically the most feasible, and Lathrop has the potential to directly impact the State Water Project's drinking water quality.

Lathrop is a small municipality that was rapidly urbanizing prior to the housing market collapse. Being able to assess its impacts on drinking water quality now will give us the opportunity to revisit later and assess the changes in land use and water quality. Also because Lathrop is a small municipality, it is covered under the Phase II General NPDES Permit and is, therefore, not required to monitor its stormwater runoff. In order to manage drinking water throughout the Delta effectively, it is necessary to know what contributions small growing municipalities make to drinking water quality.

Objectives

This study will assess the effects of urban stormwater runoff from Lathrop on the San Joaquin River Watershed with special attention paid to first flush storm water events. Because the population of Lathrop is small, this study may serve as a baseline of water quality conditions and land use patterns. As development continues to grow, we will be able to see at what population size urbanization results in significant effects on drinking water quality. This may be useful in policy decisions regarding monitoring of stormwater and mitigation of negative impacts on drinking water quality for urban runoff.

Study Design

Sampling will start at the first storm event of the 2009-2010 wet season, and will continue for at least 2 years. Grab samples will be collected from the rivers, and composite samples collected by autosamplers will be collected from the city's stormwater pumping plants.

River samples will be collected on the San Joaquin River south of Lathrop at Mossdale, north of Lathrop at Brandt Bridge, and at Lathrop just downstream of the confluence of the San Joaquin and Old River. Grab samples will also be collected at the head of Old River. Grab samples from the rivers will be collected via boat or van and the timing of collection will be determined by the tide. The order in which the river stations will be sampled will depend on what stage in the tidal cycle the river is in at that time, such as flood or ebb, and samples will be collected within a timely manner to ensure all river station samples are collected at the same stage. For example, when the storm event occurs, if the tidal stage is flood, the Brandt Bridge station would be sampled first, and the Mossdale station would be sampled last, but all stations would be sampled during the flood tide. Because storm events can occur during any stage in the tidal cycle, samples taken during separate storm events may not be comparable since samples taken at both flood and ebb tides are not comparable. Therefore, the focus of the analysis will be on what percent of the total load Lathrop contributes to the San Joaquin River.

Autosamplers will be used to collect samples from Lathrop's 8 pumping plants that discharge to the San Joaquin River. These stations are M1, M2, M3, M5, M6, KV, River and Stone Bridge pumping plants. These stations automatically pump discharge into the river once a pre-determined volume is reached in their stilling well. Figure 1 identifies both the cities' discharge stations and the river sites that will be sampled.

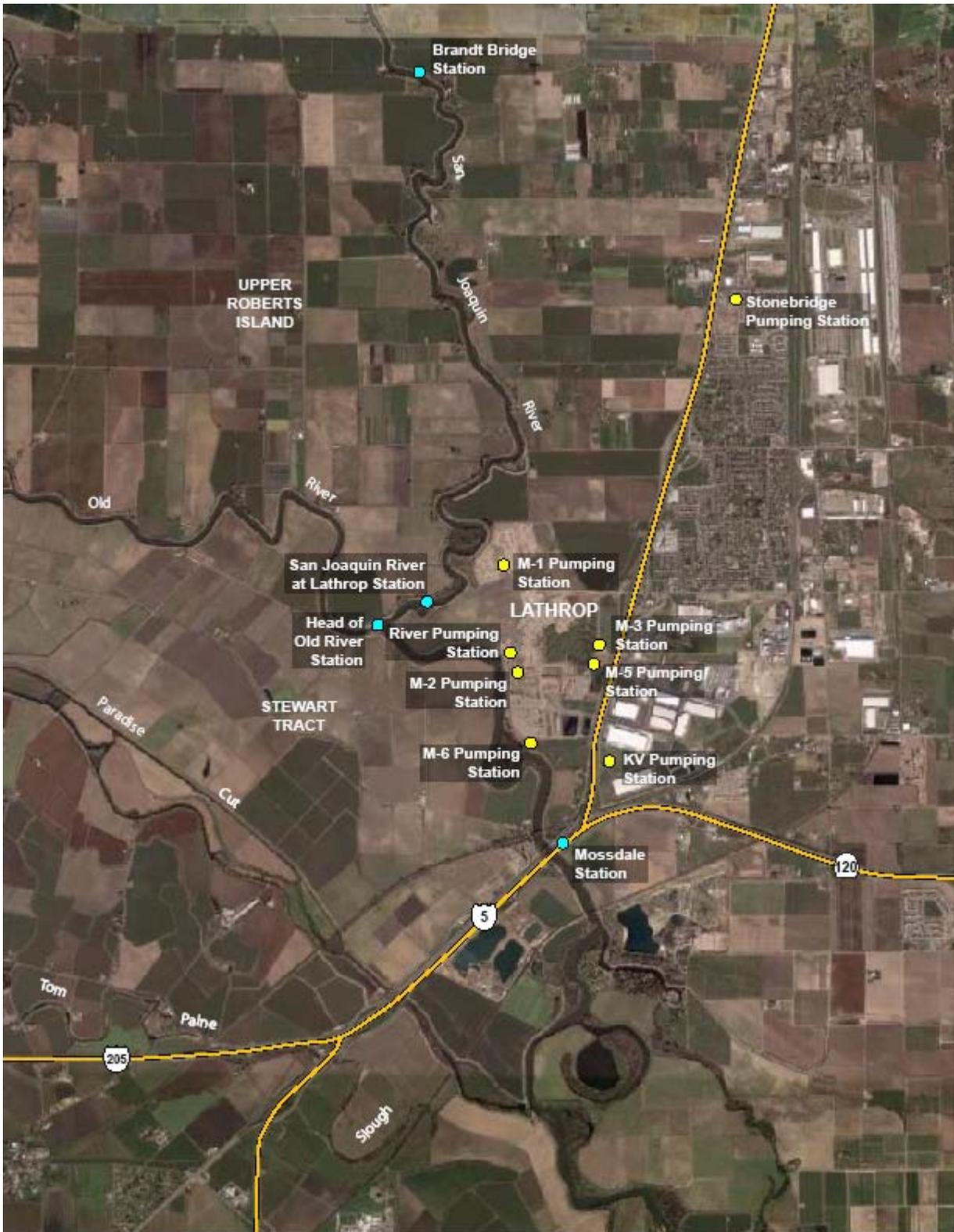


Figure 1. Location of sampling stations for urban runoff study. City discharge pump stations are in yellow. River sampling stations are in blue.

Sample analytes will include minerals (Calcium, Magnesium, Sodium, Potassium, Alkalinity, Sulfate, Chloride, Boron), metals (Aluminum, Antimony, Arsenic, Cadmium, Chromium, Copper, Iron, Lead, Mercury, Nickel, Manganese, Molybdenum, Selenium, Silver, Thallium, Zinc), nutrients (Nitrate+Nitrite, Ammonia, Organic Nitrogen and Ammonia, dissolved orthophosphate), pesticides (chlorpyrifos, diazinon, malathion, atrazine, simazine, cyanazine, prometryn), total and dissolved organic carbon, bromide, bacteria (total and fecal coliforms), turbidity, total dissolved and suspended solids, UVA₂₅₄ and total trihalomethane formation potential.

A GIS analysis will assess the land use patterns in the study area. This analysis will be valuable in a future correlation between change in land use patterns and water quality.

Deliverables and Timelines

Deliverables	Participants	Estimated Completion Date
Storm event sampling at 12 sites in the Lathrop study area	MWQI Staff MWQI Field Group	September 2011
Analysis of samples as indicated above by DWR	Bryte Laboratory	October 2011
Final Report	MWQI Staff	April 2012

Budget

See 2009/10 Workplan

2008-09 Workplan Proposal for Urban Sources and Loads Investigation--Lead Investigator: Rachel Pisor

Background/Introduction

As Delta watersheds continue to urbanize, the impacts to drinking water quality from urban runoff is of concern. MWQI has already conducted one intensive urban loading study of the Natomas East Main Drainage Canal (NEMDC) watershed. The study found that, on a daily basis, NEMDC contributed up to 93 percent of the organic carbon load in the Sacramento River at Hood during the wet season. On a monthly basis, NEMDC contributed up to 8.2 percent of the organic carbon load, up to 19 percent of the nitrate plus nitrite load, and up to 14 percent of the orthophosphate load at Hood. These numbers emphasize the level of impacts that urban drainage can have on drinking water quality and the importance of tracking urban loading as the Delta continues to urbanize.

Objectives

The purpose of this study is to investigate where MWQI should focus its efforts for another urban load study in the FY 2009/10. Possible areas of investigation include:

- a) examining the impacts from a Southern Sacramento urban watershed (ie. Morrisson Creek).
- b) conducting a follow-up study to the previous NEMDC study, with the purpose of determining whether any water quality changes have occurred in the 4 years that have passed between studies and filling in data gaps associated with the first NEMDC study.
- c) examining Stockton urban impacts to the San Joaquin River (identifying suitable sample areas).
- d) evaluating the effectiveness of mandated in-place Best Management Practices (BMPs) from stormwater permits as they relate to drinking water constituents of concern.

e) quantifying urban runoff from Brentwood and/or Lathrop as their vicinity to the Banks Pumping Plant would have the immediate impact on water quality, and because of their size, no stormwater monitoring has been conducted by the cities.

During this fiscal year, staff will examine the feasibility of the above options (and any others that are uncovered). The goal of this research is to provide the background information required to begin the field work or design of the project. Research conducted will determine the ideal location, feasibility and logistics.

Deliverables and Timelines

Deliverables	Associated Tasks	Participants	Estimated Completion Date
Conduct background research and investigate study locations, feasibility and logistics.	A,	MWQI Program	June 2009

Budget

Labor Costs: Labor hours: 1595.5 Labor Cost: \$118,128 Other Costs: 0 Total Cost: \$118,128

**2008-09 Workplan proposal for Sources, Fate, and Transport of
Nitrosamines and their Precursors in the Sacramento-San Joaquin
Delta and the State Water Project--Lead Investigator: Carol DiGiorgio
and MWDSC**

Note there are no changes between the 2008-09 study design and the 2009-10 study design. The latest study planned for 2010-11 is summarized in the 2010-11 Workplan.

Background/Introduction

Nitrosamines are highly carcinogenic compounds with cancer potentials much higher than that of trihalomethanes (THMs). Historically, nitrosamine concerns have centered on food products. More recently, interest has focused on drinking water—especially effluent-impacted supplies, as surface waters used for drinking water that are downstream of wastewater treatment plants (WWTPs) may contain the carcinogenic compounds themselves, or the precursors necessary to form nitrosamines. Depending on the level of nitrification and/or the use of advanced physical/chemical treatment at a WWTP, the discharge can be a major source of nitrosamines and/or their precursors. Treated wastewater used for groundwater recharge has been shown to contain N-nitrosodimethylamine (NDMA) at elevated levels (cited in Mitch and others, 2003). In an effluent-dominated river in Colorado, elevated levels of nitrosamines (i.e., NDMA and N-nitrosomorpholine [NMOR]) and nitrosamine precursors have been detected (Krasner and others, 2005). There is also evidence that some nitrogenous pesticides may react with chlorine or chloramines to form nitrosamines (for example, diuron) (Chen and Young, 2007). In addition, certain nitrosamines (e.g., NDMA) can be a chloramination by-product created during the drinking water disinfection process. If certain organic nitrogen precursors are present, drinking water facilities that have switched from chlorine to chloramines, to reduce THM formation in their distribution system, may find themselves in the untenable position of having reduced THMs only to have created more toxic nitrosamines.

Because it was first detected in drinking water wells, much of the attention has been directed at NDMA. However, as more information has become available, the California

Department of Public Health has set notification levels of 10 ng/L each for NDMA, N-nitrosodiethylamine (NDEA), and N-nitroso-di-n-propylamine (NDPA), with a Public Health Goal for NDMA of 3 ng/L

<http://www.cdph.ca.gov/certlic/drinkingwater/Pages/NDMAhistory.aspx>, accessed 12/29/07). The EPA's Unregulated Contaminant Monitoring Rule 2 (UCMR2) has also listed 6 nitrosamines, NDEA, NDMA, NDPA, N-nitroso-di-n-butylamine (NDBA), N-nitroso-methylethylamine (NMEA), and N-nitroso-pyrrolidine (NPYR), as contaminants to be monitored during 2008-2010 to support the Agency's determination of whether to regulate these contaminants in the interest of protecting public health <http://www.epa.gov/safewater/ucmr/ucmr2/basicinformation.html#list>, accessed 12/29/07). Early indications suggest that nitrosamines will become the next set of contaminants regulated in treated drinking water by the EPA (Bruce Macler, EPA Region 9, Pers. Comm., Oct. 2007).

The largest municipal discharger to the Delta is the Sacramento Regional WWTP, with an average annual dry weather flow of 160 MGD. Depending on its treatment practices, Sacramento Regional WWTP may be a source to the Sacramento River of both nitrosamines and nitrosamine precursors. With the plant's discharge site located a few miles upstream of a potential peripheral canal location at Hood, understanding what concentrations of nitrosamines and/or nitrosamine precursors are present at this site is critical. The next largest WWTP discharge in the Delta is located in Stockton. Although discharge from this facility (36.7 MGD average annual dry weather flow) would not affect the water quality of a peripheral canal structure, water quality at the Banks Pumping Plant could be affected. Therefore, regardless of whether a dual conveyance, a through Delta conveyance or a peripheral canal is ultimately decided upon, understanding water quality contributions from both of these WWTPs to nitrosamines and nitrosamine precursors are important to the drinking water community that receives its water from the SWP.

The potential of agricultural inputs of nitrosamine precursors (e.g., from diuron) also needs to be examined. The Delta receives pesticide and herbicide inputs from the

Sacramento and San Joaquin River's watersheds, as well as supporting an average annual farming industry of over \$2.1 billion within the Delta itself

(http://www.delta.ca.gov/pdf/Sacto-SanJoaquin_fact.pdf, accessed 12/29/07). Moreover, diuron is the third most heavily used herbicide in California.

Objectives

Because of their extreme toxicity, their likely potential to become regulated in the future, and the fact that no assessment of the occurrence of nitrosamines or the nitrosamine formation potential of Delta waters has ever been undertaken, MWQI proposes a cost share special study with Metropolitan Water District of Southern California that would 1) identify and quantify some of the potential sources of nitrosamines and their precursors at a number of key points in the Delta (i.e., sample upstream and downstream of potential point sources), and 2) examine the fate and transport of nitrosamines (which can undergo photolysis depending on the depth of the photic zone) and their precursors (which can be biodegraded to some extent in a river) in the Delta. The study proposed would be a 2-year study, so that trends and seasonal patterns could be assessed. Because this is a cost share study, no large expenditures are anticipated for this study.

Study Design

To accomplish the project objectives, MWQI would sample quarterly, for 2 years, beginning in July 2008, from 7 sites (i.e., total of 8 sampling events). The sites sampled would be:

1. West Sacramento Drinking Water Intake: This sampling site would serve as the sampling point upstream of Sacramento Regional WWTP. Samples collected at this point would also capture most of the agricultural drainage impacts from the Sacramento River watershed.
2. Sacramento River at Hood: This sampling site would serve as the sampling point downstream of Sacramento Regional WWTP and is also one of the potential sites of a peripheral canal.
3. San Joaquin River at Mossdale: This sampling site would serve as the sampling point upstream of Stockton's WWTP.

4. San Joaquin River at Holt: This sampling site would serve as the sampling point downstream of Stockton’s WWTP.
5. San Joaquin River at Vernalis: This sampling site would capture most of the agricultural drainage impacts from the San Joaquin river watershed.
6. Banks Pumping Plant: This sampling site integrates all of the Delta and riverine influences to the headworks of the SWP’s California Aqueduct.
7. Twitchell Island ag drain: This sampling site would represent the in-Delta agricultural drainage inputs from a high-carbon peat island.

Three of these sites are already part of MWQI’s discrete sampling program.

Along with standard field measurements, samples would be analyzed by Bryte Laboratory for total organic carbon, dissolved organic carbon, diuron, TKN, ammonia, nitrates + nitrites, total phosphate, UVA-254, THMFP, and HAAFP. A subset of each sample would be split and sent to Metropolitan Water District of Southern California (MWDSC)’s chemistry laboratory, where samples would be analyzed for eight nitrosamines (all nitrosamines with notification levels and all those listed in the UCMR2, as well as NMOR and N-nitrosopiperidine [NPIP]) and nitrosamine formation potential testing. If time and funding permit, MWDSC would also analyze for the anticonvulsants primidone and carbamazepine, as well as caffeine, as conservative tracers of WWTP influences. This will help determine whether the sources of the nitrosamine precursors are from treated wastewater or other sources.

Deliverables and Timelines

Deliverables	Participants	Estimated Completion Date
Quarterly sampling at 7 sites in the Sacramento-San Joaquin Delta	MWQI staff MWQI Field Group	July 2010
Analysis of all samples as indicated above by both DWR and MWDSC	Bryte Laboratory MWDSC Laboratory	August 2010
Final Report	MWQI staff MWDSC staff	December 2010
Paper for Publication	MWQI staff MWDSC staff	Submitted March 2011

Literature Cited

Chen, W.-H., and T.M. Young. 2007. Potential transformation by-product and associated risk of diuron in the disinfection process. Presented at the 233rd American Chemical Society national meeting, Chicago, Ill.

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Mitch, W. A., J. O. Sharp, R. Rhodes Trussell, R. L. Valentine, L. Alvarez-Cohen, and D. L. Sedlak. 2003. N-Nitrosodimethylamine (NDMA) as a drinking water contaminant: a review. *Environmental Engineering Science* (20)5: 389-404.

Budget.

DWR MWQI and MWDSC have agreed to a cost-sharing arrangement for this study.

2008/09 Labor Costs: Labor hours: 1144 Labor Cost: \$ 91,347 Other Costs: \$429.00
Total Cost: \$91,776

2008-09 Workplan proposal for Investigation of O'Neill Forebay water circulation--Lead Investigator: Ron Melcer

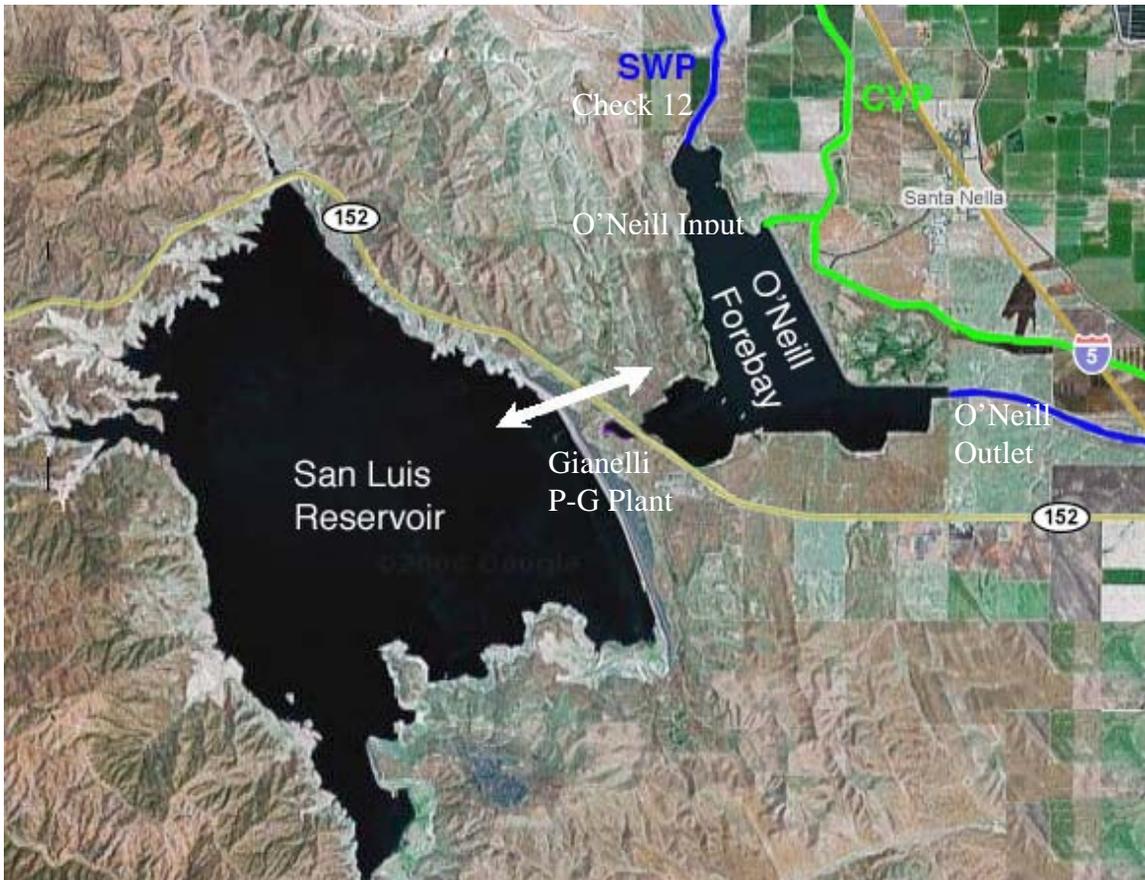
See the 2010-11 workplan for modifications to this proposal.

Background/Introduction

Water from the State Water Project (SWP) and federal Central Valley Project (CVP) are pumped into O'Neill Forebay at the foot of Sisk Dam and San Luis Reservoir (Figure 2). The SWP and CVP waters are generally of differing water quality, containing different concentrations of bromide and other dissolved salts, organic carbon, and other constituents of concern. Water from the SWP enters O'Neill at its north end, at SWP Check 12. Water from the CVP enters O'Neill on the east side, at CVP O'Neill Intake. Depending on flow and pumping conditions at Gianelli Pumping-Generating Plant, the two waters may be transported south into the joint-use aqueduct at O'Neill outlet, or flow through a channel on the west side to Gianelli and thence into San Luis Reservoir. Observations suggest that the waters do not appreciably mix in O'Neill and, specifically, that CVP water tends to hug the east shore of O'Neill and travel directly to O'Neill Outlet.

Objectives

The behavior of water flows in O' Neill forebay has important implications for water quality modeling and forecasting. The objectives of this study are to: (i) better understand water flow patterns in O'Neill Forebay under a range of conditions, (ii) support more accurate numerical modeling of the O'Neill Forebay region of the DSM2 Aqueduct Extension model, and (iii) improve forecasting of water quality characteristics in subsequent parts of the State Water Project.

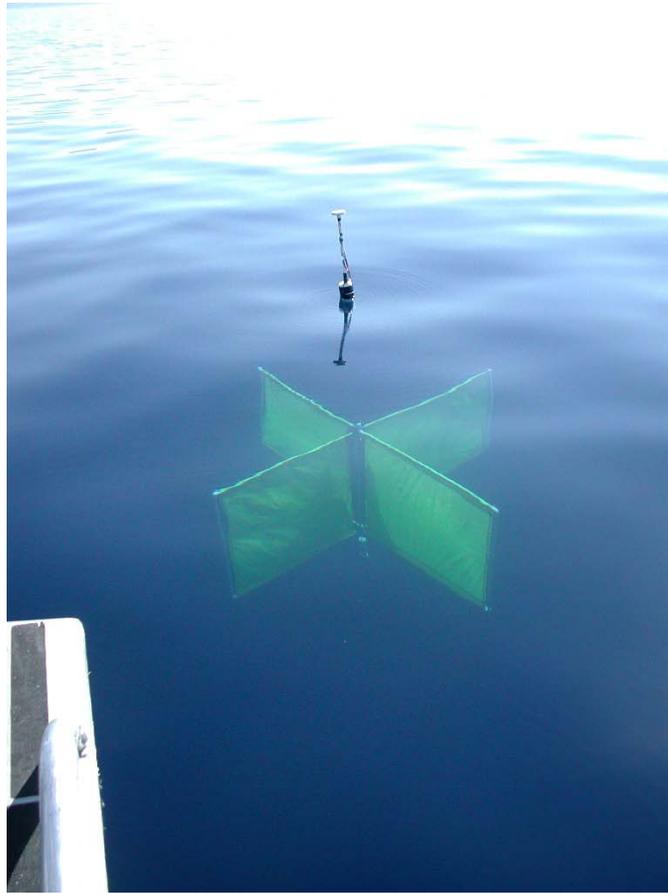


CVP water enters at O'Neill Input. The waters may not mix on their way to O'Neill Outlet.

Figure 1. Movement of SWP water into O'Neill Forebay

Study Design

Passively-drifting drogues are a proven tool in lake and ocean circulation studies (e.g., Austin and Atkinson 2004; Figure 3). A submerged “kite” moves with the water at a chosen depth, carrying a surface sensor along with it. In this application, the surface buoy would contain a small, battery-powered GPS receiver and logger. The logger would periodically record the drogue’s location for later recovery and downloading.



Buoy is attached to drogue by short stainless steel cable. Each yellow panel is 1 m square. Drifters used in this study may be much smaller. (example picture taken on Lake Tahoe, CA-NV).

Figure 2. Example of a drifter surface buoy with a GPS location logger

Deliverables and Timelines

Deliverables	Participants	Estimated Completion Date
Purchase miniature logging GPS rec and materials to construct drifters.	MWQI Program	Sept 2008
Assemble and test drifters	MWQI Program	Oct 2008
Field studies at O'Neill Forebay	MWQI Program	Dependent on pumping. Nov 2008 - May 2009, with potential sampling in July 09 based on Wanger effects on summer pumping.
Data Analysis and preparation of report	MWQI Program	Dec 2008 – June 2009
Preparation of peer-reviewed manuscript for publication	MWQI Program	May 2009 – July 2009

Literature Cited

Austin, Jay and Sten Atkinson. 2004. The design and testing of small, low-cost GPS-tracked surface drifters. *Estuaries and Coasts* 27(6): 1026-1029.

Budget

Labor Costs: Labor hours: 1559.5 Labor Cost: \$125,509 Other Costs: \$10,000 Total Cost: \$135,509

2011-12 Workplan Proposal for In-situ Fluorescence of Dissolved Organic Matter, Proof of Concept – Lead Investigators Joe Christen, Arin Conner.

Background/Introduction

This is a proof of concept of using an in-situ fluorescence measurement as a proxy for high frequency measurements of dissolved organic carbon (DOC) concentrations in the headwaters of the California Aqueduct at the H.O. Banks Pumping Plant (Banks). The study duration is to last for one year to encompass the seasonal variation in the composition of the waters.

The fluorescence properties of dissolved organic matter (DOM) in natural waters have been demonstrated to be a potential predictor of DOC concentrations (Coble 2007, Cumberland and Baker 2007, Kraus et al 2010, Smart et al 1976). Kraus et al had found the relationship between fluorescence of dissolved organic matter (FDOM) and DOC to be slightly stronger than the relationship between ultra violet absorbance at 254 nm (UVA) and DOC (Kraus et al 2010). Recent studies have used in-situ measurements of FDOM as a proxy for high frequency measurements of DOC concentrations (Downing et al 2008, Downing et al 2009, Saraceno et al 2009). The in-situ deployments demonstrated strong linear regressions between FDOM measurements and corresponding laboratory measurements of DOC; reported r-squared values ranged from 0.74 to 0.98.

Collected FDOM measurements from Banks will be used to model daily average DOC concentrations measured by the Banks Shimadzu organic carbon analyzer. Temperature and pH effects will be taken into account either as model parameters or by establishing correction curves.

Instrumentation

The fluorometer will be a Turner Designs Cyclops 7 with excitation wavelength of 350nm and an emission wavelength of 450nm, bandpasses will be 10 nm and 50 nm respectively. The 350ex/450em pair was chosen since this fluorophore is associated with humic like, and fulvic like, substances (Coble 1996), particularly ones of terrestrial,

agricultural, and anthropologic origin (Coble 2007) and was chosen after examination of preliminary data. Preliminary excitation emission matrix (EEM) data provided by Murage Ngatia from Barker Slough and Calhoun Cut have a single large intensity peak around 340ex/430em. Furthermore the 350ex/450em pair falls more within the center of the EEM region of maximum correlation with DOC from 33 samples taken in the McKenzie River, Washington (Kraus et al 2010). In that study the strongest DOC predictions from EEM's were derived in the region within 320 to 370 nm excitation and 420 to 470 nm emission (Kraus et al 2010).

The fluorometer will be positioned within the Banks water quality station and fitted with a flow thru cap. Source water filtered by a 0.45 micron membrane from the water quality station's intake system will be split to run through the Cyclops flow thru cap. Data will be collected hourly after an appropriate warm up period by a Campbell data logger. A calibration curve will be established with varying concentrations of a quinine sulfate solution.

Temperature has been shown to affect fluorescence (Smart et al 1976). To compensate for the seasonal range of temperatures at Banks curves will be established with a solution of quinine sulfate and with a source water sample.

Correction curves will not be established for pH. Fluorescence increases with pH (Patel-Sorrentino et al), but pH effects will likely be indiscernible over the typical ranges at the Banks Pumping Plant (Smart et al 1976) and indiscernible behind changes in fluorescence due to compositional changes (Coble 2007, Cumberland and Baker 2007)

Maintenance

The fluorometer lens will be cleaned weekly. Filters and lines will be maintained and maintenance activities recorded as part of the RTDF Field Support Units usual maintenance schedule. Logged data will be downloaded at a minimum of once a month.

Quality Control

The instrument's accuracy will be ascertained by a measurement of a standard solution of quinine sulfate. If the measurement relative percent difference is greater than 20% from the expected reading the data collected prior to the calibration reading will be flagged as invalid. The instrument will be recalibrated to the standard. Checks against the standard solution will be performed once a month.

QC data collected for precision and accuracy of the Shimadzu carbon analyzer as part of the RTDF program will be reviewed to insure that DOC data collected are of satisfactory quality.

Literature Cited

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Saraceno, John Franco, Brian A. Pellerin, Bryan D. Downing, Emmanuel Boss, Philip A.M. Bachand, and Brian A. Bergamaschi. 2009. High Frequency in situ Optical Measurements During a Storm Event: Assessing Relationships Between Dissolved Organic Matter, Sediment Concentrations, and Hydrologic Processes. *Journal of Geophysical Research* 114.

Smart, P.L., B.L. Finlayson, W.D. Rylands, and C.M. Ball. 1976. The Relation of Fluorescence to Dissolved Organic Carbon in Surface Waters. *Water Research* 10: 805-811.

**2011-12 Workplan MWQI Spectrofluorometer Special Study Project
Plan – Lead Investigators Ted Swift**

MWQI Spectrofluorometer
Special Study Project Plan

Prepared by
Ted Swift, MWQI

In collaboration with
MWQI Field Support Unit
Murage Ngatia, DWR QAQC Branch
James Sickman, UC Riverside
Stuart Krasner, Metropolitan Water District of Southern California

Draft Final 24 February 2011

Section 2. Introductions and Overview

Introduction

In the Sacramento-San Joaquin River Delta, sources of dissolved and particulate natural organic matter (NOM) include tributary river flows from distinct watersheds, algae and submerged vegetation growth and decay, and organic-rich peat soils. NOM concentrations and characteristics in source waters, ultimately bound for municipal drinking water use, is of great interest to water contractors and water treatment operators because of the disinfection byproducts (DBPs) resulting from water treatment.

In 2007, the DWR QA/QC group acquired a high-performance Horiba / Jobin-Yvon FluoroMax 4 spectrofluorometer to, among other uses, investigate the usefulness of spectrofluorometric analysis to Delta and Delta source waters. An extensive and growing body of literature (e.g., references in Hudson et al. 2007), strongly suggest that this approach may provide rapid methods of accurately quantifying multiple constituents of concern (COCs) in a single measurement.

This study will evaluate:

- the usefulness of spectrofluorometry as a method of rapidly quantifying constituents of concern such as DOC, algae and disinfection by-product formation potential in the Sacramento-San Joaquin Delta system;
- the potential predictive advantages of collecting detailed excitation-emission matrix data as compared to discrete excitation-emission pairs;
- identify distinctive fluorescence characteristics of Delta source waters to provide water “fingerprints” that would be used to validate Delta water quality models, among other things.

Background

Natural water sources contain a complex variety of dissolved and particulate organic materials, or natural organic matter (NOM). In the Sacramento-San Joaquin River Delta, sources include tributary river flows from distinct watersheds, in-Delta algae and submerged vegetation growth and decay, and organic-rich peat soils. NOM concentrations and characteristics in source waters ultimately bound for municipal drinking water use is of great interest to water contractors and water treatment operators because of the disinfection byproducts (DBPs) resulting from water treatment. Regulatory agencies such as the US EPA and the California Department of Public Health (DPH) have put in place regulations on the concentrations of DBPs allowable in finished drinking water.

Thus, it is of great interest to (a) understand the sources, chemical reactivity, and seasonal variations of NOM in Delta source waters and (b) identify ways of producing the most useful water quality information with the least effort and cost.

NOM can be evaluated through several surrogate measurements such as total organic carbon (TOC), dissolved organic carbon (DOC), absorbance spectroscopy (e.g., UVA254) and spectrofluorescence methods. For example, MWQI operates TOC/DOC analyzers at the two main tributary points (the Sacramento River at Hood and the San Joaquin River at Vernalis) and two export facilities (Banks Pumping Plant on the State Water Project and Jones Pumping Plant on the federal Central Valley Project). UVA254 is used by DWR O&M as a DOC surrogate at several points throughout the SWP. These have all proven to be quite useful in accurately measuring TOC or DOC as a bulk measurement. However, without other concurrent and relatively laborious analyses, such as trihalomethane formation potential (THMFP) or algal pigment analysis, these bulk measurements do not provide much insight into the sources, concentrations, and potential reactivity of NOM in a given water sample.

Fluorescence occurs when a loosely held electron within an atom or molecule is excited to a higher energy level (electron orbit) by absorption of energy, e.g, a photon of light, and subsequently releases energy as light as it drops to a lower energy level. Some energy is lost prior to emission, so the energy of the emitted photon is lower than the excitation energy. Stated another way, the wavelength of the excitation light is shorter than the emission wavelength. The wavelength at which excitation and emission occur is specific to the molecule involved. Those compounds that absorb light (often pigments) are called chromophores and those that both absorb and re-emit light energy are called fluorophores. Aromatic organic compounds provide particularly good subjects for fluorescence analysis due to the electron structure of the carbon ring (Hudson *et al.*, 2007).

A fluorometer is an instrument that excites the sample at one wavelength and measures the resultant fluorescence at a longer wavelength to measure a given suspended material, such as chlorophyll contained in algal cells. A spectrofluorometer extends that principle by exciting the sample across a rapidly-scanned range of ultraviolet-to-visible light wavelengths, while simultaneously measuring light emission across another band of wavelengths. Each matrix consists of hundreds of excitation-emission measurement combinations of a single water sample. The result is an *excitation-emission*

matrix (EEM), such as Figure A, where excitation wavelength is on one axis, emission wavelength is the second, and fluorescence intensity forms a third axis.

Water constituents of concern, such as DOC and algae, along with other characteristics that may be distinctive of each source water, can be resolved from features in the EEM (Beggs et al., 2009; Yan, 2000). For example, pigments within living algae produce distinctive features characteristic of the algal family. Spectrofluorescence has also been used to distinguish wastewaters from pristine waters (e.g., Baker *et al.* 2004b, Hudson *et al.*, 2007). A paper by Hua, et al. (2007) demonstrated that fluorescence may be useful in detecting nitrosamine precursors. In a study of the South Platte River, a major tributary in the Denver area, effluent organic matter (EfOM) has been found to be richer in dissolved organic nitrogen and precursors for nitrogenous DBPs (haloacetonitriles and nitrosamines) than the river water. (Krasner et al., 2008).

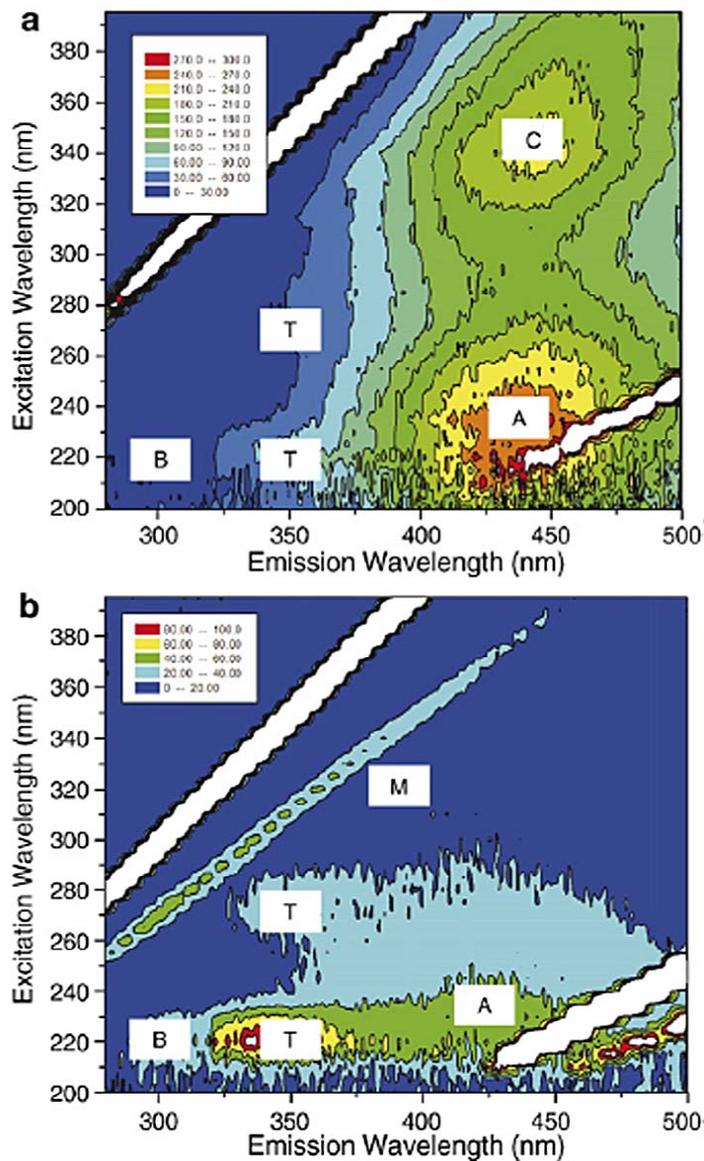


Figure A. Typical fluorescence EEMs observed in a study by Spencer et al., 2007.

Typical fluorescence EEMS showing the position of the principal fluorophores in optical space: (a) River Tyne, England (b) coastal North Sea. Note that the fluorescence intensity scale is different for (a, 0-300) and (b, 0-100). C=terrestrial humic/fulvic-like peak; M=marine humic/fulvic-like peak; A=humic-like peak; T=tryptophan-like, protein-like peak; B=tyrosine-like, protein-like peak. Fluorophores C and M are often referred to as H, humic/fulvic-like peak for comparison. The diagonal linear features are Rayleigh Tyndall and Raman scattering of water, respectively (from Spencer et al., 2007).

In 2007, the DWR QA/QC group acquired a high-performance FluoroMax 4 spectrofluorometer to, among other things, investigate the usefulness of spectrofluorometric analysis to Delta and Delta source waters. An extensive and growing literature (e.g., Beggs et al., 2009; references in Hudson *et al.* 2007), strongly suggest that this approach may provide a rapid method or methods of accurately quantifying multiple constituents of concern in a single measurement.

Structurally, this Plan is based on tools and guidance developed by R. Katznelson to assist with preparation of comprehensive and communicative Project planning documents. Other materials were also conferred with during the preparation of this Monitoring Plan.

This Plan has been prepared for the following purposes: (a) communicate with technical experts and receive their feedback and input before the monitoring resources are spent; (b) share all the important elements of the planned activities with the Technical Staff, Field Operators, and Lab staff who will be doing the actual work, at the level of detail and the specificity they need (beyond the individual SOPs); (c) establish the quality assurance and quality control (QA/QC) protocols that will be used to ensure the quality of the information generated is sufficient and documented. Thus, once approved, this Plan will provide a reference document for all operators throughout the life of the Project.

The Plan is written for a specific study effort, to be conducted within the Sacramento-San Joaquin River watershed, and is focused on specific lines of inquiry (i.e., questions of applicability, sensitivity of the approach as a novel survey method).

Beyond the Plan approval and distribution page (Section 1) and this Introduction (Section 2), the contents of the Plan are organized in the following sections.

Section 3 provides the geographical settings and explains the reason for monitoring, starting with the problem statement and culminating with the questions that the monitoring activities will attempt to answer.

Section 4 describes the organizations involved in the Project, shows the roles and functions of personnel involved in Project Tasks, and lists the other people that have input to the Project (data users, other stakeholders, and advisors).

Section 5 shows the major tasks and timelines for their completion (and refers the reader to Appendix A for details).

Section 6 reiterates the study questions and provides all the “what, where, and when” information, including the sampling design principles and the power of the dataset as required for the intended use of the data. The section also lists other sources of data and information that will augment the data sets collected for this project.

Section 7 specifies the measurement quality objectives (MQOs) and other quality objectives developed to enable the intended use of the data, and provides explanation on the data quality indicators that address these objectives.

Section 8 describes the methodology that will be used to achieve the MQOs

Section 9 is a focused Quality Assurance Project Plan that specifically addresses the way Project personnel will affect, check, record, and report the quality of the data, including accuracy, precision, resolution uncertainty, lack of contamination, lack of deterioration, and operator's competence. This section also communicates further information about data processing, including data verification and data validation, as well as about the overseeing and auditing tasks, both internal and external.

Section 10 provides a brief Health and Safety Plan for the Project.

Section 11 discusses how the data will be managed and shared, lists the data interpretation and analyses steps that may be relevant to this Project, and lays out the outline for the project's Technical Report.

Section 3. Problem Statement and Monitoring Objectives

3.1 Geographical Setting

Field grab samples will be collected approximately monthly for two years at sites in the Delta study area and Delta tributary source waters. Sites will be selected to reflect the individual tributary source waters, capture seasonal variations, and the likely sources of organic carbon and other constituents of concern in each source water. To capture a wide range of conditions and source water types while minimizing staff labor and travel costs, samples for analysis will be collected during MWQI's normal monthly field runs and by regional sample runs (e.g., North Delta run, South Delta run). Sampling stations will consist primarily of several stations regularly sampled by the MWQI Field Unit:

1. West Sacramento Drinking Water Intake. Samples from this site represent the Sacramento River upstream of Sacramento Regional Wastewater Treatment Plant (WWTP) and before the confluence with the American River. Samples here reflect most of the agricultural drainage contributions from the Sacramento River watershed.
2. Sacramento River at Hood. Samples from this site represent water downstream of Sacramento Regional WWTP and the confluence with the American River.

3. Sacramento Water Intake on the American River. Samples from this site represent water from the American River only, before it meets the larger Sacramento River.
4. Natomas East Main Drain at El Camino (NEMDC). NEMDC drains an urbanized watershed on the north side of the Sacramento metropolitan area, including urban storm-water.
5. North Fork Mokelumne River at Wimpy's Marina. Samples from this site represent the "East Side Stream" tributaries to the Delta.
6. Old River at Bacon Island. Samples from this site represent waters on the west side of the Delta which are often bound for the State and Federal export pumps, and the Contra Costa Water District "diversion" pumps. Under moderate and low river flow and significant Project pumping, water at this site would consist mostly of Sacramento River water, and sometimes a small (~1-3% by volume) amount of sea water from the San Francisco Bay. Under winter high flow conditions, this station would tend to consist of water from the San Joaquin River.
7. San Joaquin River at Vernalis. Samples from this site represent the San Joaquin River as it enters the Delta from the San Joaquin Valley to the south. It includes most of the agricultural drainage impacts from the San Joaquin Valley watershed, and seasonally receives relatively pristine waters from tributaries draining the western slope of the Sierras.
8. Banks Pumping Plant. Samples from this site represent water as it leaves the Delta at the beginning of the State Water Project's California Aqueduct.
9. Barker Slough Pumping Plant. This is the intake for the North Bay Aqueduct (NBA) that serves portions of Solano and Napa Counties. It receives water from the Sacramento River and, during the wet seasons, regional runoff exhibiting high turbidity and organic matter content.
10. Jones Pumping Plant. Samples from this site represent water as it leaves the Delta and enters the Federal Central Valley Project.
11. Colusa Basin Drain at Knights Landing. Samples from this site represent water drainage from the heavily-farmed Colusa Basin to the north and northwest of the Delta.

These are summarized in Table 1.

Table 1. Spectrofluorometer samples coordinated with MWQI Monthly Sample Runs

Site	DWR Water Data Library ID	Sample Run
Natomas East Main Drain @ El Camino (NEMDC)	A0V83671280	North Delta
American River @ Water Treatment Plant	A0714010	North Delta
Sacramento River @ West Sacramento Intake	A02104.51	North Delta
Sacramento River @ Hood	B9D82211312	East Delta
North Fork Mokelumne River @ Wimpy's Marina	B9D81371295	East Delta
Old R at Bacon Island	B9D75811344	South Delta Run
San Joaquin River @ Vernalis	B0702000	E Delta Run
Barker Slough near N. Bay Aqueduct Pumping Plant	B9D81651476	NBA Sampling
Banks Pumping Plant Headworks	KA000331	Banks Run
Jones Pumping Plant	B9C74781352	Banks Run
Colusa Basin Drain at Knights Landing	A0294500	North Delta

Physical Parameters collected at all sites: Temperature, pH, Turbidity, Dissolved Oxygen, and Specific Conductance
 Code 2 – Standard Nutrient analysis includes: Nitrate + Nitrite, Ammonia, Organic Nitrogen and Ammonia, Total Phosphorus (unfiltered)

3.2 Problem Statement

Quantification of organic carbon and other characteristics of natural source waters are labor-intensive and therefore expensive, and the analytical results are available days to weeks after sample collection. Characteristics of concern include the potential to form disinfection byproducts during the municipal drinking water disinfection process, including trihalomethanes (THMs) and haloacetic acid (HAA) from organic carbon compounds and nitrosamines from organic nitrogen compounds. There is a need to investigate methods that have the potential to reduce these costs and/or provide additional information at the same cost.

3.3 Monitoring Objective and Study Questions

This study will evaluate the usefulness of spectrofluorometry as a method of rapidly quantifying constituents of concern (COCs) such as DOC, algae and organic carbon, and as a method of fingerprinting source waters as they pass through the Delta. This study will provide MWQI staff with the opportunity thoroughly use and evaluate a bench top spectrofluorometer, which will provide important insight on the instruments structural or behavioral characteristics. In turn this will help MWQI assess the feasibility of configuring a spectrofluorometer instrument to operate unattended in real-time monitoring stations. This study will also seek to identify distinctive characteristics of

Delta source waters to provide a water “fingerprint” that would be used to, among other things, validate Delta water models.

Once the data set is assembled, it can be evaluated to address several questions. This study will evaluate:

- the usefulness of spectrofluorometry as a method of rapidly quantifying constituents of concern such as DOC, algae and disinfection by-product formation potential in the Sacramento-San Joaquin Delta system; DBPs to be investigated include THMs, HAAs, and nitrosamines.
- identify distinctive characteristics of Delta source waters to provide water “fingerprints” that would be used to validate Delta water quality models, among other things.

Presuming the methods prove useful, a potential later effort would be to evaluate the feasibility of configuring a spectrofluorometer instrument to operate unattended in real-time monitoring stations. Lines of inquiry will be implemented to answer the questions stated above. Monitoring work under this Project will be performed year-round, in support of all investigation questions.

Section 4. Project Personnel, Roles, and Responsibilities

4.1 Project Personnel

Ted Swift, Ph.D., the lead investigator, will be responsible for overall project management tasks including invoicing and reporting, coordination with Bryte Laboratory and Weck Laboratory, and oversight of project progress. He will work closely with the MWQI Field Staff and Murage Ngatia, of the DWR QA/QC group, and assure that any problems are solved promptly.

Dr. Swift will seek expert advice and review during the process of Project Planning and design, and will be responsible for the scientific defensibility of the data collection effort, for the usability of the data, and for complete documentation of data quality. He will maintain technical dialogs with advisors and experts (e.g., Prof. Jim Sickman, UC Riverside), and will be responsible for collaboration with other agencies and stakeholders active in the watershed.

Table 4-1. Project Personnel, their Roles, and Contact Information

Name	Affiliation	Role	Phone	Email
Ted Swift	MWQI	Project Lead	916-376-9718	tswift@water.ca.gov
Murage Ngatia	DWR QA/QC	QA advisor	916-376-9714	mngatia@water.ca.gov
Steve San Julian	MWQI Field Support	Field Sampling coordinator	916- 371-2284	sjulian@water.ca.gov
Sid Fong	DWR Bryte Laboratory	Laboratory Manager, Liaison	916- 375-6008	sfong@water.ca.gov
Marilyn Romero	Weck Laboratory	Lab accounting	626-336-2139	Marilyn@wecklabs.com
Alan Cheng	Weck Laboratory	Laboratory Chemist	626-336-2139	Alan@wecklabs.com
Stuart W. Krazner	Metropolitan Water District of S. Calif.	Collaborator for Nitrosamine issues	909-392-5083	skrasner@mwdh2o.com
Inge Werner, Linda Deanovic	UC Davis Aquatic Toxicology Lab	Source of Selenastrum pure algae culture	530-754-8060 530-754-6772	iwerner@ucdavis.edu, ladeanovic@ucdavis.edu
Mike Taliaferro, Doug Thompson	DWR Delta Field Division	Field Sampling at Barker Slough	209-833-2040, 209-833-2044	talafero@water.ca.gov, dat@water.ca.gov

Ted Swift and Murage Ngatia will also take care of purchasing and maintaining equipment and calibration standards, reviewing data sheets and calibration records, entering the data into electronic format, calculating measurement error, etc. MWQI Field Unit staff will be in charge of implementing Field QA procedures as described in the MWQI Field Sampling SOP. Ted Swift will conduct periodic reviews to assure fulfillment of all QA requirements.

Ted Swift will be in charge of rep-event and post-events calibrations and accuracy checks, and preparing the field sample bottles for MWQI Field Support Staff to fill. Ted will also maintain communication with Sid Fong of Bryte Laboratory, and review the laboratory analyses as they come in.

Steve San Julian will be the lead field activities person. He will assist Ted Swift in scheduling and conducting field sampling. Steve is very familiar with the Delta, and MWQI's field sampling operating procedures.

4.2 Other Parties Associated with the Project

Table 4-2 lists individuals who will be associated with the Project in various capacities but will not be Project personnel. Prof. James Sickman has collaborated with MWQI on numerous occasions in

the past, and has already suggested improvements in the monitoring design. Other interested parties include members of the Delta water quality monitoring community members who may be able to use the data and findings to gain deeper insight into Delta water quality dynamics and possible management measures.

Table 4-2. Project Advisors, Data Users, and Stakeholders

Name	Affiliation	Phone	Email
James Sickman	Assoc. Prof. Hydrology, Univ. of California, Riverside	951-827-4552	james.sickman@ucr.edu
John Coburn	Consultant to the State Water Contractors	916-316-3477	jccoburn@comcast.net
Rich Losee	RTDF New Technologies Subcommittee	909-392-5124	rlosee@mwdh2o.com

Section 5. Project Tasks and Schedule

Figure 5-1 shows the major tasks that will be undertaken, and the anticipated time line for the performance of each task. The June 2010 will be used to conduct all the preparations and training sessions needed to get ready, and put sampling routines in place (FLIMS Project IDs, etc.).

Sampling events will be conducted approximately monthly at sites in the Delta study area. There will be an interim data validation and interpretation effort as soon as data from the first sampling sets have been collected, and lessons learned will be immediately applied to refine logistics and methods for subsequent samplings, as needed. An Interim Technical Report will be submitted to the stakeholders and the advisors no later than June 30, 2011, and the final report will be completed by October 31, 2012.

Figure 5-1a. Spectrofluorometer Project Time Line for Major Tasks

Task	Aug	Sept	Jan	-	Oct	Oct	Jun
	2010	2010	2012		2012	2012	2013
Complete Project Plan and have all parties' approval							
Train & prepare spectrofluorometer routines							
Conduct Sampling & Spectrofluorometric analysis for Study							
Analysis of samples by DWR Bryte Lab, Weck Lab							
Analysis of samples by Weck Lab for THMFP and HAAFP							
Conduct data validation and prepare Interim Technical Report							
Prepare Final Technical Report							
Solicit Review, receive comments, and finalize of Technical Report							

Figure notes: Time is marked by the starting or ending times of major activities.

Figure 5-1b. Spectrofluorometer Deliverables and Timelines

Milestones & Deliverables	Participants	Estimated Start Date	Estimated Completion Date
Approximately monthly sampling at sites in the Delta study area	MWQI Staff MWQI Field Unit	Sept 2010	June 2012
Spectrofluometric analysis of raw and filtered water samples	MWQI Staff	Sept 2010	June 2012
Analysis of samples by DWR Bryte Laboratory	Bryte Laboratory	Sept 2010	June 2012
Interim report	MWQI Staff	Sept 2011	July 2011
Final Report	MWQI Staff	Oct 2012	June 2013

Section 6: Monitoring Strategy and Design

6.1 Water Quality Characteristics, Number of Samples, and Logistics Planned for this Project

Data collection will proceed along several lines of inquiry.

The central question – **“What observable features can be identified in excitation-emission matrix data that correlate highly with DBP formation and DBP precursors in drinking water?”** - will be addressed via sampling at multiple locations within the river network, followed by parallel analysis of samples for spectrofluorometric data, water characteristics of concern (DOC, TOC, THMFP, HAAFP, nitrosamine formation), and chemical constituents likely to be precursors (e.g., organic nitrogen). A growing body of literature strongly suggests that the answer to this question is “yes” (e.g., Hua et al. 2007, Henderson et al, 2009, Hudson et al, 2007).

A second question is: **“Does detailed excitation-emission matrix data provide significantly more information leading to prediction of DBP formation than data from a small set of excitation-emission wavelength pairs produced by submersible fluorometers (e.g., Turner Designs)?”**

Laboratory preparations of specific “end member” waters will include dissolved organic carbon from known Delta peat soil, pure cultured algae, and cultured algae that has been allowed to senesce.

Field activities will be led by MWQI Field Support staff, and lab analyses will be performed at Bryte Laboratory and Weck Laboratory (THMFP and HAAFP). In coordination with the MWQI standard field sampling program, samples will be analyzed by Bryte Laboratory for total organic carbon, dissolved organic carbon, pH, UVA-254, THMFP, and HAAFP.

Both the total and dissolved fractions of water samples will be analyzed spectrofluorometrically with the Fluoromax 4. UV254 absorbance will also be measured as part of absorbance spectra measurements using the Field Unit's Hach spectrophotometer. Split samples will also be analyzed by Bryte Laboratory for TOC, DOC, nitrate, nitrate, total ammonia, and TKN (these are part of the "nutrient" group routinely analyzed in the MWQI grab-sample monitoring plan). THMFP and HAAFP will be performed by Weck Laboratories under contract with Bryte Lab.

Nitrosamine formation potential will be analyzed by MWD as part of a separate project lead by Carol DiGiorgio. Split field samples from that study will be analyzed spectrofluorometrically to determine if nitrosamine precursor artifacts are detectable in the EEM data. To date, nitrosamines themselves have not been detected in source waters by Ms. DiGiorgio's project. However, nitrosamines result from reactions, in the disinfection process, with organic nitrogen species present in source waters. Some of these organic nitrogen compounds may fluoresce at distinctive locations in the EEM, thus providing a link between nitrosamine formation potential and characteristics that can be observed in the source waters.

The resulting data will be analyzed to identify distinctive features in the EEMs that are highly correlated with characteristics such as DOC and TOC concentration, THMFP, HAAFP, nitrosamine formation, and algal biomass. Analytical tools will include multiple regression (e.g., Marhaba et al., 2003), parallel factor analysis (Parafac, e.g., Steadman and Bro, 2008; Teymouri, 2007), and principle component analysis (PCA, papers by Leibovici), with emphasis on the first two. Principal component analysis (PCA) will be used to evaluate similarities and differences between sample sites and uncover general patterns, using PTAK software within the R software system to deal with the multidimensional nature of the EEM data (Leibovici and Sabatier, 1998, Leibovici, in press). However, Steadman and Bro (2008) point out that PCA characterizations tend to be qualitative, rather than quantitative, and the resulting principal components are mathematical abstractions that do not lend themselves to direct chemical interpretation.

Software tools will include MS Excel for basic planning and sample tracking, Origin software for instrument control and preliminary data organization, the R System for Statistical Computing, the N-Way Toolbox (Andersson and Bro, 2000) operating within the Octave open-source software package (Alsberg and Hagen, 2006), and Minitab statistical software.

In support of question 2, data at discrete excitation-emission pairs will be abstracted from the set of larger EEM matrix data and evaluated against the constituents of concern data using regression analysis.

Expected results will include identification of excitation-emission fluorescence peaks that correlate highly with specific constituents of concern, including measures of precision such as confidence intervals for constituent concentration predicted from fluorescence, correlation coefficients (R-squared values), and p-values. The traditional 95% confidence will be used to report statistical significance. However, observed features with p-values larger than 0.05 will be reported in cases where they show practical applicability (e.g., explain a large fraction of the variability as measured by R-squared).

Once the methods are well characterized, their efficacy as part of the routine monitoring will be evaluated and be presented to the MWQI TAC with recommendations.

Field measurements will be performed using a variety of meters, electrodes, or probes operated by the MWQI Field Support Unit.

Sample containers will be prepared and delivered to the field crews before each sampling event. The containers will have a label with placeholder for the Sample ID, Station ID, Date, time, and operator initials; the operators will fill out this label before filling the container with sample water. All samples will be collected using MWQI SOPs, including tracking within Bryte Laboratory's FLIMS data system.

Water samples will be delivered to Ted Swift, Bryte Laboratory, and Weck Laboratory for respective analysis. Appropriate sample preservatives will be added to the containers before sample collection or as appropriate for the specific measurement protocol. Further detail on the instruments and methods to be used are provided in Section 8 below.

Samples will be analyzed as soon as possible after collection to minimize for the possibility of sample changes or deterioration. However, Yan *et al.* (2000) found in a study of sample stability that a sample that had been stored in a sealed dark-glass container for 43 days had, within experimental error, same structure and fluorescent intensity originally measured for those samples within 24 h of collection.

Laboratory study of algal culture

Celenastrum is a commonly cultured green alga used in ecotoxicology bioassays. Ted Swift will acquire a pure culture by arrangement with the UC Davis Aquatic Toxicology Laboratory (Contacts: Linda Deanovic, Inge Werner). The sample will be split, and a subsample analyzed immediately, following the protocols described above. Two subsamples will be allowed to age and senesce, and small subsamples from these will be analyzed at intervals representing realistic time-scales found in the Delta (e.g., 2 days, 5, days, 14 days). One of the subsamples will be wrapped in aluminum foil to exclude light to simulate environmental conditions found below the euphotic zone and hasten senescence.

Table 6-1: Parameter Package and Logistics in support of study questions for the Spectrofluorometer Special Study

Measurement Intent	Characteristics (Parameter package)	Personnel	Activity type	Activity Frequency and Interval	Time of Day	Weather & flow conditions	# of Station Visits
Field conditions	pH, water temperature	MWQI Field Staff	Field measurements	Approx. monthly	Any	Any	24 planned (2 years of 12 monthly samplings collecting at 12 sites; 288 samples)
OC DBP precursors	Dissolved & Total Organic Carbon	Bryte Laboratory	Sample; lab analysis	Approx. monthly	Any	Any	“
Organic N DBP precursors	TKN	Bryte Laboratory	Sample; lab analysis	Approx. monthly	Any	Any	“
Organic N DBP precursors	Total ammonia	Bryte Laboratory	Sample; lab analysis	Approx. monthly	Any	Any	“
Inorganic N DBP precursors	Nitrate, Nitrite	Bryte Laboratory	Sample; lab analysis	Approx. monthly	Any	Any	“
DBPFP	THMFP	Weck Labs	Sample; lab analysis	Approx. monthly	Any	Any	“
DBPFP	HAAFP	“	Sample; lab analysis	Approx. monthly	Any	Any	“
DBPFP	Nitrosamine Formation Potential	MWD	Sample; lab analysis	Approx. monthly	Any	Any	12 planned (1 year of N samplings collecting at M sites).

Sampling trips will be conducted approximately monthly, as part of the MWQI monitoring program, supplemented by sampling at targeted locations such as the North Bay Aqueduct intake at Barker Slough; exact timing (the specific day within the week or the season) will be determined based on water quality conditions, and Field Unit schedule. Unfortunately the time of day will not be selected deliberately, for logistical reasons, because each sampling run consists of visiting multiple sampling locations during one sampling day. Monitoring work will be performed during daylight only, but the data may be augmented with results of wet-weather monitoring.

The total number of samples for the Project may reach 244 or more, depending on number of stations sampled, the end-member supporting studies, and the number of replicates. The MWQI Field Crew visits twelve stations as part of the routine monitoring program. Several of these stations tend to exhibit low seasonal variation (e.g., American River), however, and other stations will be substituted (e.g., Barker Slough Pumping Plant). The field crew will collect a sample volume sufficient to meet the needs of the several analyses. The crews will perform sampling events approximately monthly during the Project. In summary, each Station will be sampled 12 times per year. Please note that additional samples will be collected as field duplicates, and sets of sample containers will also be filled with clean water to serve as field blanks.

6.2 Sampling Design Principles Used to Select Locations and Timing

Sampling stations are selected with the intent of representing a significant tributary to the Delta, an important export location from the Delta, or a site of known wide variation. The timing of sampling will be selected with the intent of capturing seasonal variation and significant hydrologic or biological events within the constraints of staff resources and safety. None of the Stations was or will be selected at random. The sampling design principle used to select stations is ‘directed’, meaning that location were selected based on MWQI’s knowledge of the watershed. The season was also selected using the ‘directed’ sampling design principle, but unfortunately it is impossible to select the time of day deliberately because the crews will have to visit multiple stations in one day. Thus, different Stations will end up representing different times in the day.

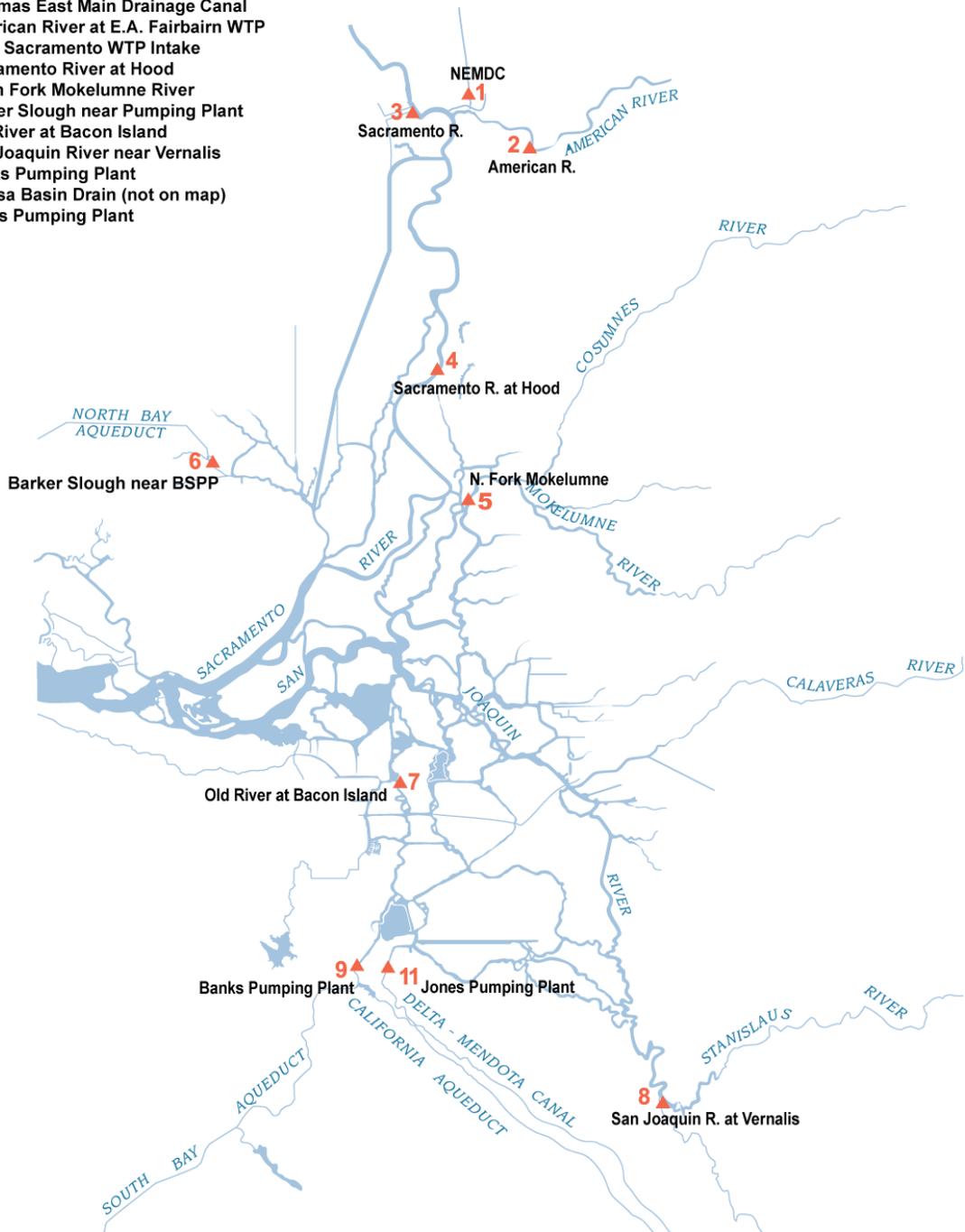
6.3 Sampling Station Location

The Sacramento – San Joaquin River Delta consists of a river network at the confluence of these two main rivers, along with several other smaller “East Side” rivers, and several sloughs on the north and south sides. Figure 6.1 shows the planned sampling locations on a map of the watershed with the major waterways and selected landmarks.

Planned sampling stations will be selected from a list of established sampling locations, mapped by GPS coordinates, and described by landmarks. All these points will be listed and documented in the Location spreadsheet of the Project File (the MS Excel workbook prepared for this project).

Figure 6-1 Spectrophotometer study sampling locations

1. Natomas East Main Drainage Canal
2. American River at E.A. Fairbairn WTP
3. West Sacramento WTP Intake
4. Sacramento River at Hood
5. North Fork Mokelumne River
6. Barker Slough near Pumping Plant
7. Old River at Bacon Island
8. San Joaquin River near Vernalis
9. Banks Pumping Plant
10. Colusa Basin Drain (not on map)
11. Jones Pumping Plant



6.4 Other Sources of Data and Information

Data collected by the field staff will be augmented by noteworthy observations of local conditions, e.g., algal blooms , distinctive water appearance.

Section 7: Measurement Quality Objectives (MQOs)

Data acquisition activities will include both field measurements and laboratory analyses, and the quality objectives depend on the amount of error that can be tolerated. However, data collected for this Project has the potential of being used for additional purposes in conjunction with other data sets collected by other investigators (e.g., Prof. Jim Sickman), and the quality objectives selected for the Project have been refined to reflect this. The quality objectives for field measurements are listed in Table 7-1: Table 7-2 shows the quality objectives for laboratory analyses.

Table 7-1 – Measurement Quality Objectives and Other Quality Objectives for Field Measurements

Study question or intent	Characteristic (Parameter)	Unit	Accuracy (unit or Percent) (Note a)	Precision (unit or RPD) (Note a)	Resolution	Target Reporting Limit	Completeness
Source ID	pH	pH	± 0.2	± 0.2	0.1	N/A	90%

Note a: Unit or percentage, whichever is greater.

RPD – Relative percent Difference – is the difference between two repeated measurements expressed as a percentage of their average.

N/A – not applicable

Table 7-2 shows the quality objectives for all quantitation activities that will take place at Bryte Laboratory and Weck Laboratory.

Table 7-2: - Measurement Quality Objectives (MQOs) and Other Quality Objectives for Laboratory Analyses

Characteristic (Parameter)	Unit	Accuracy (or LCS Recovery)	Precision RPD	Matrix Spike Recovery	Target Reporting Limit	Completeness
TKN	mg N/L	± 85-125 %	± 20 %	74-127%	0.1	90%
Total Ammonia	mg N/L	± 85-125 %	± 20 %	86-118%	0.1	90%
DOC and TOC	mg N/L	± 30 %	± 30 %	80–120%	0.5	90%
THMFP	ug/mg	± 85-125 %	± 20 %	N/A	0.1	90%
HAAFP	ug/mg	± 85-125 %	± 20 %	N/A	0.1	90%
Nitrosamine Formation	ug/mg	± 85-125 %	± 20 %	N/A	0.1	90%

RPD – Relative Percent Difference – is the difference between two lab replicates (sample or spikes) or two field duplicates, expressed as a percentage of their average.

LCS Recovery –Laboratory Control Sample in clean water. Note: CRM (Certified Reference Material) solutions usually come with specified recovery limits and confidence level and the Project’s quality objective is to meet those.

Most of these values are taken from the Bryte Chemical Laboratory Quality Assurance Manual, May 2006 (DWR, 2006).

Section 8: Instruments and Methods for Field Measurements and Laboratory Analysis

This section describes the measurement systems that will be used to collect the data for the Spectrofluorometer Special Study. Each measurement system has typical capabilities and limitations, i.e., can attain a given level of accuracy and precision, and these “performance criteria” were consulted in the process of instrument/method selection.

The measurement systems selected to achieve the Measurement Quality Objectives (MQOs) developed for field and lab measurements are shown in Table 8-1. These instruments will be described in detail in the Instruments spreadsheet of the Project File (the MS Excel workbook prepared for this project). Different types of instruments for field measurements may be used, provided that all types used have adequate resolution and are capable of achieving the MQOs.

Measurement systems that involve sampling and analysis have a set of specifications that must be followed in order for the system to achieve its performance criteria and yield valid data. The following two tables provide information about the measurement systems that will be used for the Project. The information table related to field and storage operations (sample handling) is presented in **Table 8-2**.

Table 8-1 Instruments and Kits Used for Field and Lab Measurements

Characteristic (Parameter)	Method base	Type /Method	Features	Model	Calibration Mode	Range and Units	Resolution
pH	EPA 150.1	Dry electrode	Pocket meter without ATC	Various	automatic (pH 4,7,10)	0 to 14 pH units	0.1
Fluorescence				Jobin-Yvon Fluoromax-4	Manual and automatic	Relative fluorescence	
Absorption				Hach	Manual and automatic	Absolute absorption	0.001 A
Dissolved Organic Carbon	EPA 415.1	Chemical Oxidation		OA-XXX	manual	0 to 10 mg/L (lab dilutes)	0.05 mg/L
THMFP	EPA 510.1					ug/mg	ug/mg
HAAFP	EPA 552.2					ug/mg	ug/mg
Nitrosamine formation						ug/mg	ug/mg

Table 8-2: Specifications for Sample Handling

Characteristic	Method #	Method group	sample container material & property	minimum container volume (ml)	preservative	holding time (at 4 deg C)
Total Organic Carbon	EPA 415.1	Oxidation	Glass	100	Phosphoric	28 days
Dissolved Organic Carbon	EPA 415.1	Oxidation	Glass	250	Phosphoric to pH<2	28 days
pH	EPA 300.0		Plastic or glass	500	None	28 days
THMFP	EPA 510.1		Plastic or glass	500	None	14 days
HAAFP	EPA 552.2		Plastic or glass	500	None	14 days

Section 9: Quality Assurance Plan

This section describes how the quality of the measurement data collected during this effort will be assured. Good data depends on competent operators, good capture of all supporting documentation, and effective protocols. These three factors are described below. The procedures to affect and check data quality are described next, followed by the procedures for recording and reporting the quality of the data generated by each of the measurement systems. The section also communicates further information about data processing, including data verification and data validation, as well as about the oversight and auditing tasks, both internal and external.

9.1 Competent Operators

Field operators' competence will be assured via training (awareness and skills) as part of the MWQI Field Support operating procedures. All samples will be collected under the direction oversight of experienced environmental scientists familiar with MWQI SOPs. All Project personnel will seek out materials and courses that will help them to fulfill their roles. Dr. Swift and Mr. Ngatia have received introductory training on the Fluoromax 4 instrument and the Origin control software used to operate it and collect and organize its data. They have also taken several courses in environmental statistical analysis, and will take additional classes if the need arises and time permits. The Projects will not utilize a formal certification process, though several previously taken courses did produce attendance certificates.

9.2 Documentation

Documentation of Project data will proceed throughout the life of the Project, using hardcopy field data sheets, the Bryte Lab's Field and Laboratory Information Management System (FLIMS), laboratory notebooks and MS Excel spreadsheets developed as part of the data quality management (DQM) system for local Projects.

All Project information will be entered into the appropriate spreadsheets related to each research question. Station locations, Project personnel names, roles, and contact information, field equipment, and calibration standard solutions will be entered into a

project management spreadsheet. Laboratory data will be imported in electronic format into the Project Data spreadsheet, and information captured in the hardcopy field data sheets discussed below will be entered Field Data spreadsheet along with a Calibration & Accuracy Checks spreadsheet.

Field activities will be recorded on the Field Data Sheets tailored to this Project, which include placeholders for the Station visit identifiers, the visual observations, the field measurements, and the sampling log. Some of the field crews may opt to capture all information called for in the Field Data Sheet in electronic format while at the Station, using a personal digital assistant (PDA).

Calibration and accuracy check records for field instruments will be captured on the appropriate data sheet as part of existing MWQI Field Unit protocol. Each Instrument has a unique Instrument ID that will be used to track its performance.

The calibration and accuracy checks records on the data sheet will include the following:

- Date, Time, Reason (pre-event or post event)
- Instrument ID
- Standard Material, if applicable
- 'True' Value of Standard Material
- Reading of the Instrument before any adjustments
- Adjustments and outcome
- Operator
- Electrode voltage for instrument performance checks (for Sonde probes)

The concept of a unique Instrument ID has been implemented in the DQM for documenting the quality of field and lab measurements, because it links a set of measurement results with the calibration records of the instrument that was used to collect them. Other bits of information will also be linked via a unique ID, including Sample ID, Station ID, Dataset ID, and Operator Name

9.3 Protocols

Field operators using instruments with multiple probes (e.g., YSI or Hydrolab Sondes) will follow manufacturer's instructions and MWQI protocols. For pocket meters,

Operators will use instrument-specific procedures with detailed instructions for ways to affect/check/record/report (**ACRR**) data quality. Each procedure provides directions for the following actions:

- Affect (act to influence the outcome)
- Check (test to evaluate or verify)
- Record (keep everything documented), and
- Report (communicate the data quality [indicator outcome](#)).

Bryte Laboratory and Weck Laboratory will use established SOPs and protocols for each procedure and method.

9.4 Procedures to Affect and Check Quality

There are several distinct aspects of data quality and each one calls for different types of actions. Table 9-1 shows different aspects of data quality that need to be addressed for general project performance, field measurement, sample handling, and lab analyses. The aspect of operator's competence, which is pertinent to all activities, is addressed by training and proficiency checks as described above in Section 9.1. Action regarding other aspects are discussed below.

Table 9-1: Summary of Actions to Affect and Check the Performance of the Project's Measurement Systems

Activity	data quality aspect	Affect (<i>act to influence outcome</i>)	Check (<i>test to evaluate or verify</i>)
All	operator's competence	train, refresh, supervise	run proficiency tests, review work products
Field Measurement	accuracy (<i>Note 1</i>)	calibrate (adjustable-reading instruments)	conduct accuracy check (all instruments)
	precision	use consistent procedures under same conditions	repeat measurements
Sample handling	lack of contamination	decontaminate sampling equipment and containers, seal & wrap samples	collect and analyze blanks (Trip, Field, Equipment)
	lack of deterioration	ship cold; preserve if appropriate	measure shipping temperature, pH upon arrival
Lab analyses	accuracy (<i>Note 1</i>)	calibrate, use certified calibrator Standards	run LCS, CRM, Matrix spikes, surrogates
	precision	use consistent procedures under same conditions	run lab replicates, matrix spike duplicates
	lack of contamination	decontaminate lab ware	analyze lab Blanks (method, reagent, etc.)
	lack of deterioration	analyze within holding time	calculate

(Note 1) General ways to control accuracy for all field measurements and lab analyses -
 Use certified standards for calibration and accuracy checks
 clean the instrument, kit, test tube, cuvette or lab ware before and after each use
 protect all field and lab equipment and standards from extreme temperature, sunlight, excessive humidity, harmful liquids or vapors, etc.

9.4.1 Accuracy

One of the ways which will be used to assure accuracy of field measurements is frequent instrument calibration, as specified in Table 9-2 below. It is the most effective way to minimize the instrument's drift from the calibrated state. In the laboratory, accuracy will be assured by calibration using reliable standards, and will be checked via matrix spikes recovery and in the lab SOPs.

Sensitivity accuracy calibration of spectrofluorometer: The two most commonly used methods of fluorometer sensitivity calibration involve either a quinine sulfate dilution series, or normalizing observed fluorescence data to the intensity of the pure-water Raman scattering peak (Nelson and Coble, 2009). Pure water fluorescence EEM data will

be collected at the beginning of each day's sample analysis. A quinine sulfate dilution series of EEMs will be collected quarterly.

Table 9-2 describes the frequency of Calibrations and Accuracy Checks for field instruments, and the frequency of repeated measurements in the field. Because measurement accuracy is as accurate as the Standards used for instrument calibration, instrument operators will only use standard solutions that are:

- certified, or traceable to NIST or ASTM
- used within expiration date
- stored in the dark at non-extreme temperature, never frozen
- compared with fresh standards before used up

Table 9-2: Frequency of Calibration Adjustments & Accuracy Checks and of Repeated Measurements for Field Instruments

Character-istic	mode	Instrument name or type	Standard Material	Frequency of Calibration & Accuracy checks	Frequency of repeated measurements
pH	Adjust-able	Pocket pH meter (dry electrode) or Probe	Standard buffer solution, pH 4, 7, 10	Daily, calibration adjustment before first and accuracy check after last measurement	20% or 2 per trip

Table 9-3 Frequency of Checks for Sample Integrity, Laboratory Accuracy, Laboratory Precision, and Process Reproducibility.

Characteristic	Unit	Method #	Trip/Field blank frequency	Equipment blank frequency	field duplicates frequency	Lab Control Sample (LCS) type/range and check frequency	Matrix Spike /MS Duplicate frequency	Sample lab replicates frequency
Ammonia, total	mg/L	EPA 350.1	5% or 1 per Sample Batch	1 per Sample Batch	10% or 1 per Sample Batch	1 per Lab Batch (Note 2)	4 per Project	10% or 2 per Lab Batch
Nitrate, Nitrite	mg/L	SM 4500-NO3-F DWR	5% or 1 per Sample Batch	1 per Sample Batch	10% or 1 per Sample Batch	1 per Lab Batch (Note 2)	4 per Project	10% or 2 per Lab Batch
Total Kjeldahl Nitrogen	mg/L	EPA 351.2 [1]	5% or 1 per Sample Batch	1 per Sample Batch	10% or 1 per Sample Batch	1 per Lab Batch (Note 2)	4 per Project	10% or 2 per Lab Batch
THMFP	ug/mg	EPA 551.1	5% or 1 per Sample Batch	1 per Sample Batch	10% or 1 per Sample Batch	1 per Lab Batch (Note 2)	4 per Project	10% or 2 per Lab Batch
HAAFP	ug/mg	EPA 551.1	5% or 1 per Sample Batch	1 per Sample Batch	10% or 1 per Sample Batch	1 per Lab Batch (Note 2)	4 per Project	10% or 2 per Lab Batch
Organic Carbon	mg/L	EPA 415.1 Ox	5% or 1 per Sample Batch	1 per Sample Batch	10% or 1 per Sample Batch	1 per Lab Batch (Note 2)	4 per Project	10% or 2 per Lab Batch

Note 1: A Sample Batch is made of all samples collected by one Field Crew during one trip.

Note 2: A Lab Batch is made of all the samples analyzed in one day by one lab instrument between calibrations.

9.4.2 Precision

Good precision of field measurements will be achieved via awareness training and checked via repeated measurements. Laboratory precision will be enhanced by training and checked via lab replicates and matrix spikes duplicates. The reproducibility of the entire sampling and analysis process will be assessed by analyzing the field duplicate samples (field duplicates will be collected in a separate container but at the same time

and location). Tables 9-2 and 9-3 show the frequency of precision checks for the field and the lab, respectively.

9.4.3 Sample Integrity

Before and during field operations, sample integrity will be assured by decontamination of sampling equipment and training operators on all aspects of the sampling process and available equipment. Actions to assure lack of contamination will include implementing decontamination procedures, use of clean trays to place caps, and use of other devices to separate samples from contamination. Lack of deterioration will be assured by careful attention to sample cooling, shipping and storage. Sample integrity will be checked by collecting and analyzing trip blanks, field blanks, equipment blanks, and/or rinsates (if relevant). The frequency of blank samples is shown in Table 9-3 as well.

In the laboratory, sample preparation and analytical procedures will be conducted per good laboratory practices including cleaning of lab ware, analysis within holding time, protecting it from contamination as needed, sample storage at 4 deg C. Lack of contamination will be checked by collecting and/or analyzing filter blanks, test tube blanks, reagent blanks, etc.

9.5 Procedures to Record and Report Quality

The tools developed for information-capture in the field as described in Section 9.2 above, will be used to record all the quality checks conducted for field measurements and all the measurement results including repeated measurements. The same spreadsheets will also be used to calculate and report the accuracy and precision of field measurements as described below.

Accuracy will be calculated from calibration records as captured on the data sheet and/or spreadsheet. The difference between the instrument's reading and the Standard value will be calculated and recorded. This value, the "instrument drift", will be used to report accuracy in measurement units (e.g., for pH) or as a percentage of the true value of the Standard (Standards will be selected at values that are as close as possible to expected ambient values).

Laboratory LCS, surrogates, and MS recoveries will be recorded, and recovered concentration will be reported as, the percent of the nominal concentration spiked using a similar formula.

Precision will be recorded as pairs of repeated measurement results (for field measurements) and as paired results of two replicate aliquotes (or matrix spike and matrix spike duplicate) for lab analyses. Precision will be reported as RPD – Relative Percent Difference, the difference between the two samples in each pair, expressed as a percentage of their average. If there are several pairs of repeated measurements taken with the same instrument at the same event, the worst case scenario RPD for that instrument will be reported with the results collected during that event with that instrument. Selecting the widest error will assure the data user that “it probably does not get worse than this”.

Detection Limit and Reporting limits will be recorded and reported for each result point (i.e., for each sample) if sample matrix presents interference that increases them (i.e., decreases the sensitivity of the analysis).

Resolution: Records on the resolution of field instruments are already shown (reported) in Table 8-1 above and in the Instruments spreadsheet: Resolution is very relevant to field equipment with poor resolution, which drives the range of error/uncertainty around each measurement.

Sample integrity: The results of blanks representing each batch of samples will be evaluated and data batches will be flagged as needed. Results of analyses made beyond holding time will be flagged as well.

9.6 Data Verification and Validation

The process of data verification involves checking whether all monitoring activities have been performed as required and planned, all samples have been properly tracked, accounted for, and analyzed, and all the Results data have been recorded and entered correctly. This process has to start in the field. The process of data validation is about

assuring that all the measurement systems were functional and operated within their performance criteria. Beyond these two processes there is a process of data quality assessment, i.e., looking at what the validation outputs actually mean in terms of our ability to use the data, and looking for ways “to do it better next time”.

Table 9-4 show the major phases in the data verification and validation process as will be undertaken for the Spectrofluorometer study after each monitoring event. The MS Excel data quality management tools described in Section 9 above will be used to perform the steps and attach the final qualifiers to each Result. Completeness will be assessed after data inventory and validation.

Table 9-4: Phases and Tasks of Processing Water Quality Monitoring Data

Function	Phase	Phase #	Example of Tasks	Means/tools	Outcome or output
Verification	Inventory	1.1	Tally sites, Station visits, Samples, number of each type of Quality Checks, etc	Field Data Sheets, Calibration and Accuracy checks records, lab reports, etc.	Inventory of monitoring Results and quality checks
Verification	Monitoring Plan comparisons	1.2	Compare activities inventory w Plan	Inventory from Phase 1.1 and planning documents	Extent of compliance of QA actions and quality check frequencies with planning document
Verification	Alignment and matching	1.3	Align Stations with Samples, Instruments and Calibration and Accuracy checks records	Field Data Sheets, Chain of Custody records, container labels, Calibration and Accuracy checks records, etc	Verified IDs, consistent records
(Transfer)	Data entry, upload, and conversion	1.4	Type data, prepare batches for upload	Data Entry Forms or spreadsheets, upload tools	FLIMS, Project File, or Database
Verification	Correctness Check (for manual data entry)	1.5	Run spot-check or full check for data entry errors, or utilize double-entry tools	Eyes (checks) or macro (double-entry)	Correctness evaluator (per entry batch or entry operator)
Validation	Sample validation	2.1	Summarize blank checks outcome, Review field notes	lab reports regarding blanks	Sample Integrity Report chapter with narrative of findings
Validation	Error Calculation	2.2	Calculate accuracy and precision by Instrument or lab batch	Calibration and Accuracy checks records and repeated measurements records, lab QA reports (matrix spikes & duplicates etc.)	Max RPD (a measure of imprecision) and % inaccuracy per Field Instrument use period: RPDs and % recovery per lab batch.
Validation	Performance acceptability assessment	2.3	Compare error to lab control chart for each Measurement System; review detection/reporting limits	output of phase 2.1, output of phase 2.2; Field notes Re: instrument response, lab reports	Extent of compliance with performance criteria of each batch of each measurement system; % completeness
Validation	Validity status assessment	2.4	Compare output of phase 2.2 with Project's Measurement Quality Objectives (MQOs).	Outputs of phases 2.1, and 2.2	Validity Status Qualifier

Notes: 'QA Actions' include calibration and decontamination: 'Quality Checks' include all samples and checks done to document accuracy, precision, and sample integrity;

RPD (relative percent difference): the difference between two repeated measurements divided by their average times 100.

Table 9-5: Result qualifiers for this Project’s data.

Qualifier	Definition
Unknown	Information for review is not available
Not Checked	Data quality has not been reviewed
Not Valid ("NV")	Existing information indicates that the result was obtained in an analytical run or test that were not acceptable, or with the use of malfunctioning instrument
Estimated ("J")	"J"; by best professional judgment - not valid but flaw not detrimental; result can be used but with caution.
Valid	Measurement system met its performance criteria: e.g., Analytical run or test was acceptable; recoveries were within control chart, positive/negative control results were acceptable, instrument was functional, sample integrity was preserved.
Valid and meets Project MQOs	Result was valid and accuracy & precision error was within the measurement quality objectives specified for the dataset; dataset met completeness objective.

Table 9-5 shows the verbal categories to be used as Result qualifiers for this Project’s data, and the definition of each option.

As mentioned in Section 8 above, each measurement system (MS) has its own set of acceptance or performance criteria. The Laboratories have established lab control charts for all the methods they will be using to analyze this Project’s samples. The data review will include comparison of accuracy, precision, and detection limit performance for each lab batch to the MS performance criteria (e.g., is the recovery within the lab control chart) and data that met these criteria will be classified as Valid. Results from batches that did not, but can still be used with caution, will be classified as “estimated”. Data with unknown validity status will not be used for this Project, nor will the RCD use data that were rejected.

Many Projects have multiple datasets (a dataset is a group of results that share the same intent, design, and measurement quality objectives (MQOs)). If we keep in mind that the measurement systems (MS) that were selected for the datasets in this Project should be able to generate data that meet the MQOs of these datasets, it is obvious that data that meet MS performance criteria would also meet dataset MQOs.

9.7 Internal and External Review of Adherence to QA/QC Procedures

Field activities will be overseen by Mr. San Julian assisted by Dr. Swift, and in some cases by other Project personnel. They will audit the field operations on at least one event and conduct spot-checks for proficiency. Apparent lack of skill in using a given Instrument or collecting a sample will be noted, data collected by that field crew for that parameter will be flagged, and those field staff will receive training as soon as possible.

Lessons learned, protocol deviation, QA/QC results, and data validation outcomes will be compiled and reported in the Interim and Final Reports and tracked in the lab notebooks. These reports will be prepared by the Lead Investigator, and be submitted to the MWQI Branch Chief, independent advisors, and stakeholders.

9.8 Administrative Reports

Quarterly Progress Report will be prepared by the Lead Investigator and sent to the MWQI Branch Chief. Monthly progress will be briefly reported to the MWQI TAC via MWQI's internal project reporting system and verbally via the monthly conference call.

Section 10 Health and Safety Plan

This section describes the activities and the tools implemented to assure health and safety (H&S) of all Project Field Operators. Bryte Laboratory and Weck Laboratory have their own H&S Plans.

10.1 Health and Safety Responsibilities

Staff health and safety are an integral part of DWR daily operations, in field, lab and office settings. The field sampling protocol consists of the same sampling methods followed by Field Unit staff during their routine sampling programs. Within these, the basic safety policies include:

- Assuring that personnel carry out H&S practices in Occupational Safety and Health Administration (OSHA), state and local safety regulations.
- Maintenance and update of the H&S binder
- Upkeep of Material Safety Data Sheets (MSDSs) Binder
- Providing initial training and mandatory retraining of all field personnel
- Documentation of all training, including signature sheets when appropriate

- Communication of any new safety and injury prevention practices
- Purchase of safety equipment and training field operators how to use it
- Briefing of all field operators about H&S before each trip to reinforce the need to put safety above samples
- Assuring that no one goes to do field work alone
- Assuring availability of the chemist to do sample acidification at the staging area after each event

Additionally, all Municipal Water Quality Program Branch staff will conduct their work in a manner consistent with the Branch Injury and Illness Prevention Plan.

10.2 The Health and Safety Binder

A dedicated H&S Binder has already been established for DWR field operations, and this binder holds permanent information related to all field activities. The H&S Binder will reside at the MWQI Field Support trailers at Bryte Laboratory. The binder will contain the following types of items:

- Maps showing nearest hospital and quickest route to it from key locations, plus alternative routes
- Map showing location of police HQs, fire department, and other emergency resources
- All contact information of emergency resources
- Map showing areas of concern or potential hazards as gleaned in the reconnaissance activities and updated over time
- Checklists: vehicle safety, H&S equipment, etc.
- MSDSs of chemicals routinely used in the field
- Instructions for chemical spill, automotive accident and personal injury response

10.3 Disposal of Hazardous Materials

The laboratory optical analyses performed Dr. Swift and Mr. Ngatia will involve only natural water. Some of the chemical analyses performed by Bryte Laboratory and Weck Laboratory may produce waste products that require careful disposal. The laboratories have SOPs in place to properly dispose of these waste products.

10.5 Special procedures

Field operators may be responsible for adding concentrated acids or other chemicals as preservatives to sample containers. Samples will be acidified in the staging area by trained personnel using appropriate equipment and wearing appropriate protective gear (goggles, gloves, etc.). Personnel will work in well-ventilated areas and avoid inhalation of preservatives at all times.

Section 11 Data Management, Interpretation, and Reporting

11.1 Data Integration and Management

Documented, validated and qualified data generated in this Project will be stored in the Project File as described in sections 9.2 and 9.6 above. Selected information fields will be exported to one or more of the following data repositories: A local database, in Origin, MS Excel or MS Access, as appropriate, that holds data collected from field measurements and laboratory analyses. The local database will be maintained by the Lead Investigator and will be mined for data interpretation and presentation, using sort/filter commands or queries.

11.2 Statistical Analyses

Monitoring results generated in this project will be grouped according to what they represent in the environment (e.g., stream or outfall) and descriptive statistics such as average or median will be derived if meaningful. The nature of this study includes the need for hypothesis testing and for statistical comparisons between two or more “populations” of data, and the appropriate tests (e.g., t-test, ANOVA, non-parametric significance tests, multiple regression analysis) will be applied as appropriate. Analysis of correlations will be widely used to discover relationships between different characteristics (e.g., fluorescence peaks, nitrosamine formation and organic nitrogen concentration) across space and time. Fluorescence EEM data will be further analyzed using the Open Source statistical packages “R” and Octave (an Open Source version of the commercial software MatLab), along with analytical packages developed for these programs.

11.3 The Scientific (Technical) Report

Technical Report will be prepared by the Technical Leader with input from the technical experts who assisted with the study design. The report will be submitted to the MWQI Branch Chief and other stakeholders.

The Technical Report will include the following Sections:

1. Introduction: background, problem, objective, question
2. Location and methods
3. Results and discussion: Project findings, how they may be related to each other, and what they might mean in combination with data collected by others
4. Conclusion and Recommendations: Result main point, major conclusion from this study, and recommendations for next study or management measure implementation activities based on this study and other data.
5. References

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2010-11 Workplan Proposal for Spectrofluorometer Investigation--Lead Investigator: Ted Swift

Note that this study proposal updates the 2009-10 study proposal listed in this appendix.

Background/Introduction

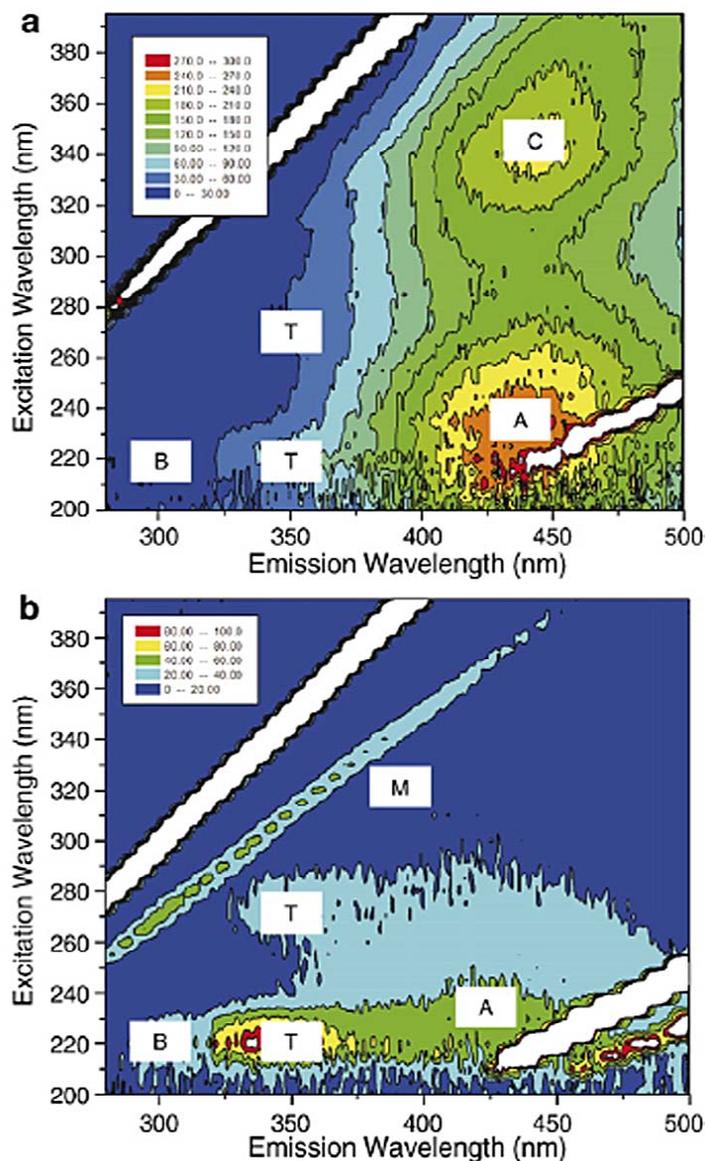
Natural water sources contain a complex variety of dissolved and particulate organic materials, or natural organic matter (NOM). In the Sacramento-San Joaquin River Delta, primary sources include tributary river flows from, in-Delta algae and submerged vegetation growth and decay, and organic-rich peat soils. NOM concentrations and characteristics in source waters ultimately bound for municipal drinking water use is of great interest to water contractors and water treatment operators because of the disinfection byproducts (DBPs) resulting from water treatment. Regulatory agencies such as the US EPA have put in place regulations on the concentrations of DBPs allowable in finished drinking water. Thus, it is of great interest to (a) understand the sources, chemical reactivity, and seasonal variations of NOM in Delta source waters and (b) identify ways of producing the most useful water quality information with the least effort and cost.

NOM can be evaluated through several surrogate measurements such as total organic carbon (TOC), dissolved organic carbon (DOC), absorbance spectroscopy (e.g., UVA254) and spectrofluorescence methods. For example, MWQI operates TOC and DOC analyzers at the two main tributary points (the Sacramento River at Hood and the San Joaquin River at Vernalis) and two export facilities (Banks Pumping Plant on the State Water Project and Jones Pumping Plant on the federal Central Valley Project). UVA254 is used by DWR Division of Operations and Maintenance (O&M) as a DOC surrogate at several points in the SWP. These have all proven to be quite useful in accurately measuring TOC or DOC as a bulk measurement. However, without other concurrent and relatively laborious analyses, such as trihalomethane formation potential (THMFP) or pigment analysis, these bulk measurements do not provide much insight into the sources, concentrations, and potential reactivity of NOM in a given water sample.

Measurement principles

Fluorescence occurs when a loosely held electron within an atom or molecule is excited to a higher energy level (electron orbit) by absorption of energy, e.g, a photon of light, and subsequently releases energy as light as it drops to a lower energy level. Some energy is lost prior to emission, so the energy of the emitted photon is lower than the excitation energy. Shorter wavelengths of light correspond to higher photon energies. Thus, stated another way, the wavelength of the excitation light is shorter than the emission wavelength. The wavelength at which excitation and emission occur is specific to the molecule involved. Those compounds that absorb light (often pigments) are called chromophores and those that both absorb and re-emit light energy are called fluorophores. Aromatic organic compounds provide particularly good subjects for fluorescence analysis due to the electron structure of the carbon ring (Hudson *et al.*, 2007).

A spectrofluorometer is an instrument that implements this principle by exciting the sample across a rapidly-scanned range of ultraviolet-to-visible light wavelengths, while simultaneously measuring light emission across another band of wavelengths. The result is an *excitation-emission matrix* (EEM), such as Figure 12, where excitation wavelength is on one axis (most often vertical), emission wavelength is the second, and fluorescence intensity forms a third axis, often represented by color. Each matrix consists of hundreds of excitation-emission measurements of a single water sample. Water constituents of concern, such as DOC and algae, along with other characteristics that may be distinctive of each source water, can be resolved from features in the EEM (Yan, 2000). For example, pigments within living algae produce distinctive features characteristic of the algal family. Spectrofluorescence has also been used to distinguish wastewaters from pristine waters (e.g., Baker *et al.* 2004b, Hudson *et al.*, 2007).



Typical fluorescence EEMs showing the position of the principal fluorophores in optical space: (a) River Tyne, England (b) coastal North Sea. Note that the fluorescence intensity scale is different for (a, 0-300) and (b, 0-100). C=terrestrial humic/fulvic-like peak; M=marine humic/fulvic-like peak; A=humic-like peak; T=tryptophan-like, protein-like peak; B=tyrosine-like, protein-like peak. Fluorophores C and M are often referred to as H, humic/fulvic-like peak for comparison. The diagonal linear features are Rayleigh Tyndall and Raman scattering of water, respectively (from Spencer et al., 2007).

Figure: 1. Typical fluorescence EEMs observed in a study by Spencer et al., 2007

In 2007, the DWR QA/QC group acquired a high-performance FluoroMax 4 spectrofluorometer to investigate the usefulness of spectrofluorometric analysis to Delta and Delta source waters. An extensive and growing body of literature (e.g., Beggs *et al.*, 2009, and references in Henderson *et al.* 2009 and Hudson *et al.* 2007), strongly suggest that this approach may provide a rapid method or methods of accurately quantifying multiple constituents of concern in a single measurement.

Objectives

This study will evaluate the usefulness of spectrofluorometry as a method of rapidly quantifying constituents of concern (COCs) such as DOC, algae and organic carbon, and as a method of fingerprinting source waters as they pass through the Delta. This study will examine the feasibility of configuring a spectrofluorometer instrument to operate unattended in remote real-time monitoring applications. It will also seek to identify distinctive characteristics of Delta source waters to provide a water “fingerprint” that would be used to, among other things, validate Delta water models.

Study Design

Field grab samples will be collected approximately monthly for two years at sites in the Delta study area and Delta source waters. Sites will be selected to reflect the individual tributary source waters, seasonal variations, and the likely sources of COCs in each source water. Sampling stations will include

- West Sacramento Drinking Water Intake. Samples from this site would represent the Sacramento River upstream of Sacramento Regional Wastewater Treatment Plant (WWTP). Samples here would also include most of the agricultural drainage impacts from the Sacramento River watershed.
- Sacramento River at Hood. Samples from this site would represent water downstream of Sacramento Regional WWTP
- Sacramento Water Intake on the American River.
- San Joaquin River at Vernalis. Samples from this site would capture the San Joaquin River as it enters the Delta. It would include most of the agricultural drainage impacts from the San Joaquin river watershed.
- Banks Pumping Plant. Samples from this site would represent water as it leaves the Delta at the beginning of the State Water Project’s California Aqueduct.
- Other source waters further upstream of the Delta, such as the Colusa Basin Drain, tributaries to the Sacramento River, the Mokelumne and Cosumnes Rivers, and tributaries to the San Joaquin River.

Samples will be analyzed as soon as possible after collection to minimize changes. However, Yan *et al.* (2000) found in a study of sample stability that a sample that had been stored in a sealed dark-glass

container for 43 days had, within experimental error, same structure and intensity originally measured for those samples within 24 hours of collection.

Laboratory preparations of specific “end member” waters will include dissolved organic carbon from known Delta peat soil, pure cultured algae, and cultured algae that has been allowed to senesce.

In coordination with the MWQI standard field sampling program, samples will be analyzed by Bryte Laboratory for total organic carbon, dissolved organic carbon, pH, and UVA-254,. Subsamples from the ongoing collaborative investigation of nitrosamine sources by Carol DiGiorgio, Joe Christen (DWR), Stuart Krasner (MWD), and others, will be analyzed spectrofluorometrically to seek out fluorescence features that correlate with nitrosamine formation potential. To date, nitrosamines themselves have not been found in detectable concentrations in field samples. However, their precursors may be detectable using these methods.

The resulting data will be analyzed to identify distinctive features in the EEMs that are highly correlated with characteristics such as DOC and TOC concentration, THMFP, nitrosamine formation potential, and algal biomass. Analytical tools will include multiple regression, parallel factor analysis, and principle component analysis.

Deliverables and Timelines

Milestones / Deliverables	Participants	Estimated Start Date	Estimated Completion Date
Sampling at sites in the Delta study area, development of lab pure samples	MWQI Staff MWQI Field Unit	March2010	June 2012
Spectrofluometric analysis of raw and filtered water samples	MWQI Staff	March2010	June 2012
Analysis of samples by DWR Bryte Laboratory	Bryte Laboratory	March2010	June 2012
Interim report	MWQI Staff	May 2011	July 2012
Final Report	MWQI Staff	July 2012	October 2012

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Budget

See 2010/11 Workplan

2009-10 Workplan Proposal for Spectrofluorometer Investigation--Lead Investigator: Ted Swift

Background/Introduction

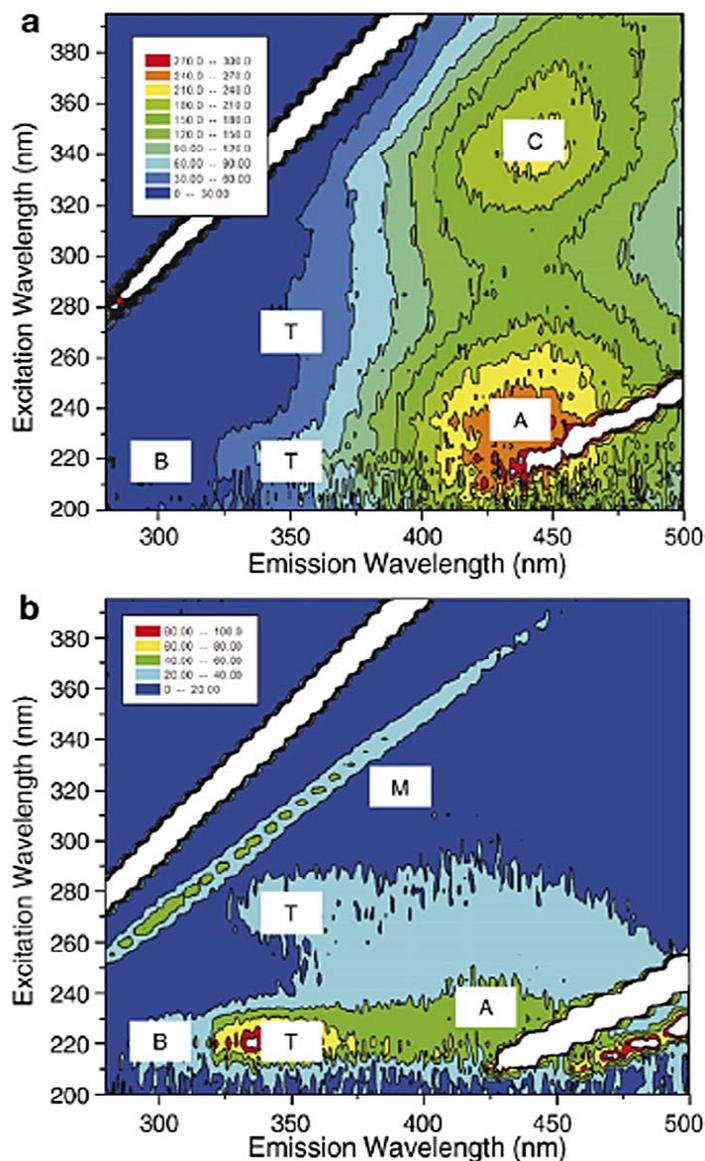
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are called chromophores and those that both absorb and re-emit light energy are called fluorophores. Aromatic organic compounds provide particularly good subjects for fluorescence analysis due to the electron structure of the carbon ring (Hudson *et al.*, 2007).

A fluorometer is an instrument that excites the sample at one wavelength and measures the resultant fluorescence at a longer wavelength to measure a given suspended material, such as chlorophyll contained in algal cells. A spectrofluorometer extends that principle by exciting the sample across a rapidly-scanned range of ultraviolet-to-visible light wavelengths, while simultaneously measuring light emission across another band of wavelengths. The result is an *excitation-emission matrix* (EEM), such as Figure 12, where excitation wavelength is on one axis, emission wavelength is the second, and fluorescence intensity forms a third axis. Each matrix consists of hundreds of excitation-emission measurements of a single water sample. Water constituents of concern, such as DOC and algae, along with other characteristics that may be distinctive of each source water, can be resolved from features in the EEM (Yan, 2000). For example, pigments within living algae produce distinctive features characteristic of the algal family. Spectrofluorescence has also been used to distinguish wastewaters from pristine waters (e.g., Baker *et al.* 2004b, Hudson *et al.*, 2007).



Typical fluorescence EEMs showing the position of the principal fluorophores in optical space: (a) River Tyne, England (b) coastal North Sea. Note that the fluorescence intensity scale is different for (a, 0-300) and (b, 0-100). C=terrestrial humic/fulvic-like peak; M=marine humic/fulvic-like peak; A=humic-like peak; T=tryptophan-like, protein-like peak; B=tyrosine-like, protein-like peak. Fluorophores C and M are often referred to as H, humic/fulvic-like peak for comparison. The diagonal linear features are Rayleigh Tyndall and Raman scattering of water, respectively (Spencer et al., 2007..

Figure 1. Typical fluorescence EEMs observed in a study by Spencer et al., 2007

In 2007, the DWR QA/QC group acquired a high-performance FluoroMax 4 spectrofluorometer to, among other things, investigate the usefulness of spectrofluorometric analysis to Delta and Delta source waters. An extensive and growing literature (e.g., references in Hudson *et al.* 2007), strongly suggest that this approach may provide a rapid method or methods of accurately quantifying multiple constituents of concern in a single measurement.

Objectives

This study will evaluate the usefulness of spectrofluorometry as a method of rapidly quantifying constituents of concern (COCs) such as DOC, algae and organic carbon, and as a method of fingerprinting source waters as they pass through the Delta. This study will examine the feasibility of configuring a spectrofluorometer instrument to operate unattended in real-time monitoring stations. It will also seek to identify distinctive characteristics of Delta source waters to provide a water “fingerprint” that would be used to, among other things, validate Delta water models.

Study Design

Field grab samples will be collected approximately monthly for two years at sites in the Delta study area and Delta source waters. Sites will be selected to reflect the individual tributary source waters, seasonal variations, and the likely sources of organic carbon in each source water. Sampling stations will include

- West Sacramento Drinking Water Intake. Samples from this site would represent the Sacramento River upstream of Sacramento Regional Wastewater Treatment Plant (WWTP). Samples here would also include most of the agricultural drainage impacts from the Sacramento River watershed.
- Sacramento River at Hood. Samples from this site would represent water downstream of Sacramento Regional WWTP
- Sacramento Water Intake on the American River.
- San Joaquin River at Vernalis. Samples from this site would capture the San Joaquin River as it enters the Delta. It would include most of the agricultural drainage impacts from the San Joaquin river watershed.
- Banks Pumping Plant. Samples from this site would represent water as it leaves the Delta at the beginning of the State Water Project’s California Aqueduct.
- Other source waters further upstream of the Delta, such as the Colusa Basin Drain, tributaries to the Sacramento River, the Mokelumne and Cosumnes Rivers, and tributaries to the San Joaquin River.

Samples will be analyzed as soon as possible after collection to minimize changes. However, Yan *et al.* (2000) found in a study of sample stability that a sample that had been stored in a sealed dark-glass

container for 43 days had, within experimental error, same structure and intensity originally measured for those samples within 24 h of collection.

Laboratory preparations of specific “end member” waters will include dissolved organic carbon from known Delta peat soil, pure cultured algae, and cultured algae that has been allowed to senesce.

In coordination with the MWQI standard field sampling program, samples will be analyzed by Bryte Laboratory for total organic carbon, dissolved organic carbon, pH, UVA-254, THMFP, and HAAFP.

The resulting data will be analyzed to identify distinctive features in the EEMs that are highly correlated with characteristics such as DOC and TOC concentration, THMFP, and algal biomass. Analytical tools will include multiple regression, parallel factor analysis, and principle component analysis.

Deliverables and Timelines

Milestones / Deliverables	Participants	Estimated Start Date	Estimated Completion Date
Approximately monthly sampling at sites in the Delta study area	MWQI Staff MWQI Field Unit	July 2009	June 2011
Spectrofluometric analysis of raw and filtered water samples	MWQI Staff	July 2009	June 2011
Analysis of samples by DWR Bryte Laboratory	Bryte Laboratory	July 2009	June 2011
Interim report	MWQI Staff		July 2010
Final Report	MWQI Staff		October 2011

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Budget

See 2009/10 Workplan